

# Lawrence Livermore National Laboratory

## Fuel Research Review

MACCCR Fuels Research Review  
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# Support from:

- DOE Office of Vehicle Technologies
  - Gurpreet Singh
  - Kevin Stork
- DOE Office of Basic Energy Sciences
  - Wade Sisk
- DOD Office of Naval Research
- Bill Pitz, Marco Mehl, Mani Sarathy   LLNL group  
and Chitral Naik, Reaction Design



# The fuel situation in 1922 looks pretty familiar

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- Thomas Midgley, Chief of Fuels Section for General Motors, 1922
  - US Geological Survey -- 20 years left of petroleum reserves
  - Production of 5 billion gallons of fuel in 1921
- Potential new sources of petroleum
  - Oil shale
  - Oils from coal
  - Fuels from biomass
- Higher efficiency a high priority for conservation reasons
  - People will not buy a car “lacking in acceleration and hill climbing”
  - Solution is higher compression ratio, then at about 4.25 : 1
  - Obstacle is engine knock, whose origin is unknown
  - Result was development of TEL as antiknock
  - **Phenomenological picture with no fundamental understanding**



# Status report on kinetics of practical fuels

- Many groups are developing mechanisms for small and large molecule fuels
- Possible to build a reasonable mechanism for nearly any fuel, using computer-generated or manually-generated techniques
- Mechanism reduction is becoming very efficient
- New need for “Mechanisms 2.0”



# Kinetic mechanisms are usually only as good as they need to be

- Early example from 1976 conference
  - $\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$
  - “This reaction and its rate must be correct because methane won’t ignite without it”
- Eventual solution
  - $\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$  Warnatz
- There are many ways to get the right answer if the question is a simple one
- Butler ‘Norris’ in “The Big Sleep” –
  - “I make many mistakes”

# Early CH<sub>4</sub> and CH<sub>3</sub>OH mechanisms

- Key pairs of reactions had estimated rate expressions
  - $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$
  - $\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$
  - $\text{CH}_2\text{OH} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$
  - $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$
- Early rates for these reactions were wrong by large margins, but their ratios were correct, and eventually experiments and theory provided better rates

# Very recent paper on methane pyrolysis

- Interested in cracking, H<sub>2</sub> production, cooling applications
- Tried existing mechanisms from Dean, GRI-Mech, Leeds, Konnov, Sung, San Diego, Dagaut, Nancy, Sandia, Glarborg, Frenklach, Milano, MIT, LLNL
  - None were satisfactory, according to authors
- Authors were looking for detailed species production, including coke formation, surface effects, small mechanisms

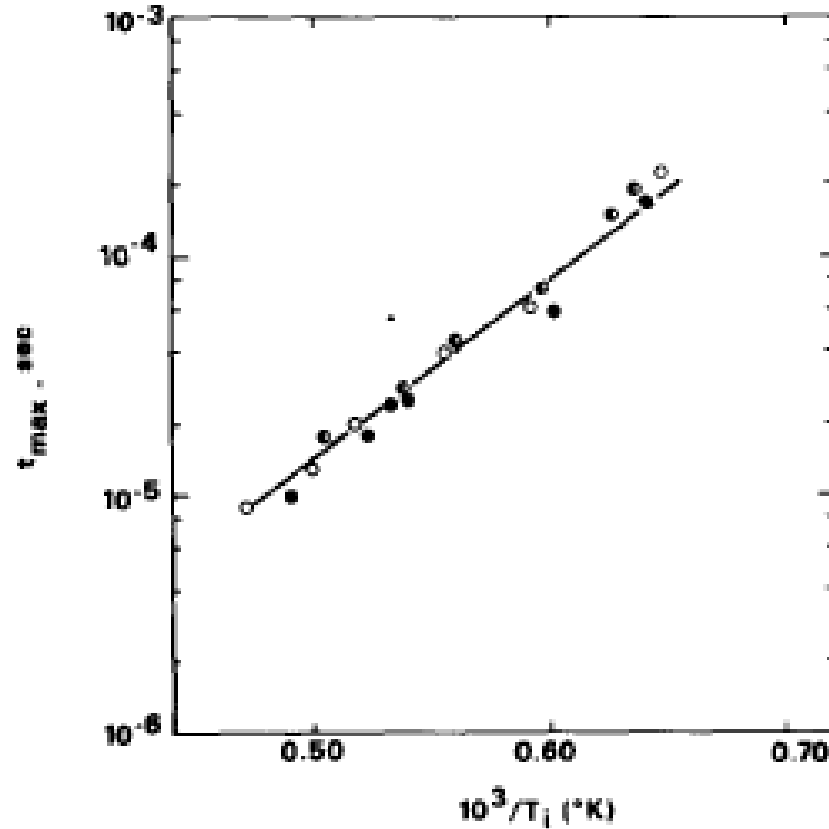
# Another example: n-heptane as a Diesel surrogate

- $CN = 56$  for  $n-C_7H_{16}$
- n-heptane makes soot
- Lots of papers used  $n-C_7H_{16}$  mechanism for diesel
- Wait a minute! Diesel fuel has lots of aromatics
- New diesel surrogates have toluene or xylene or some other aromatics
- Another issue: variation in ignition with pressure isn't quite correct, others?
  - Olefin kinetics are probably not correct



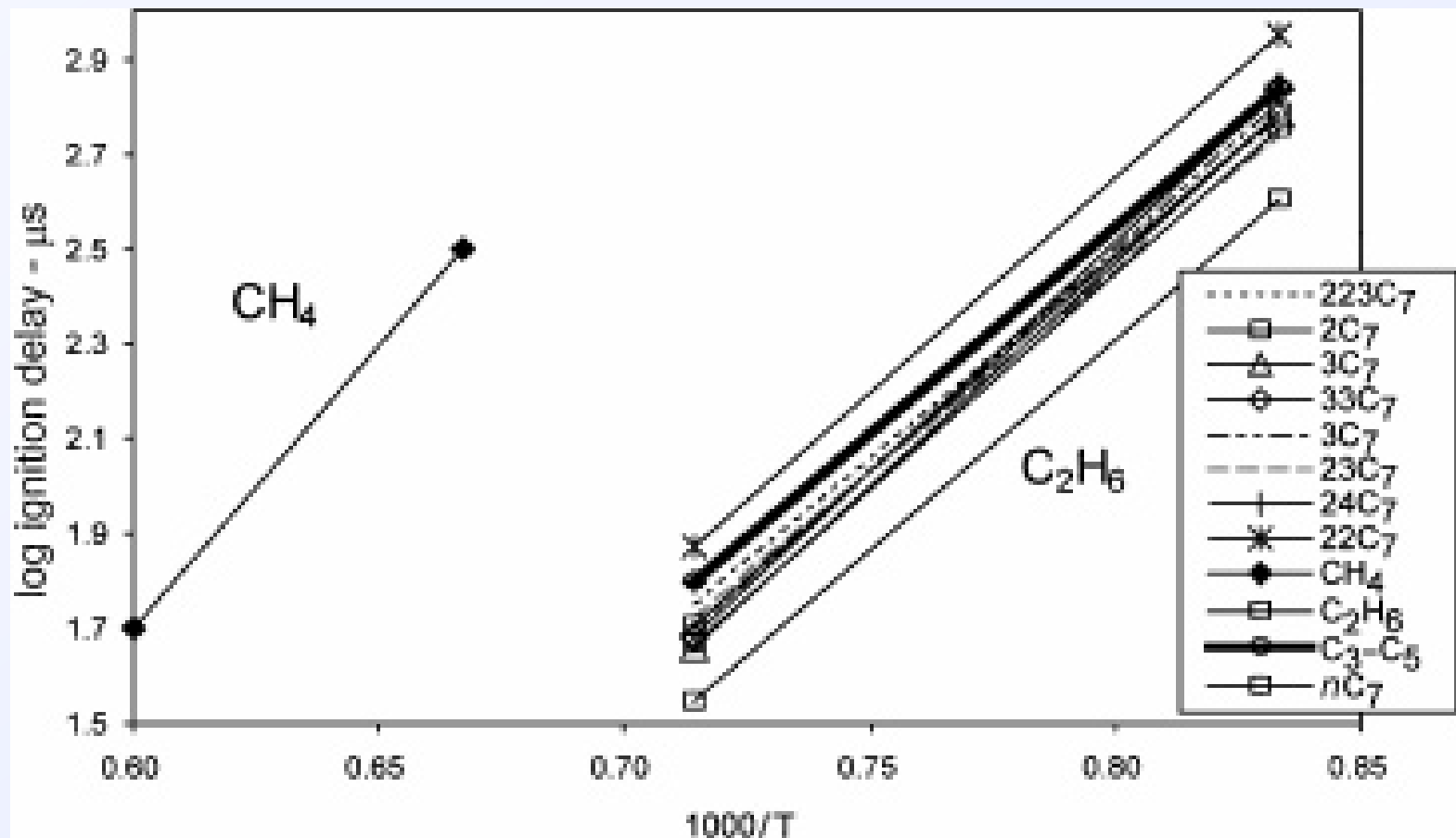
# High temperature ignition in shock tubes

Bowman, C&F 1975



methanol ignition

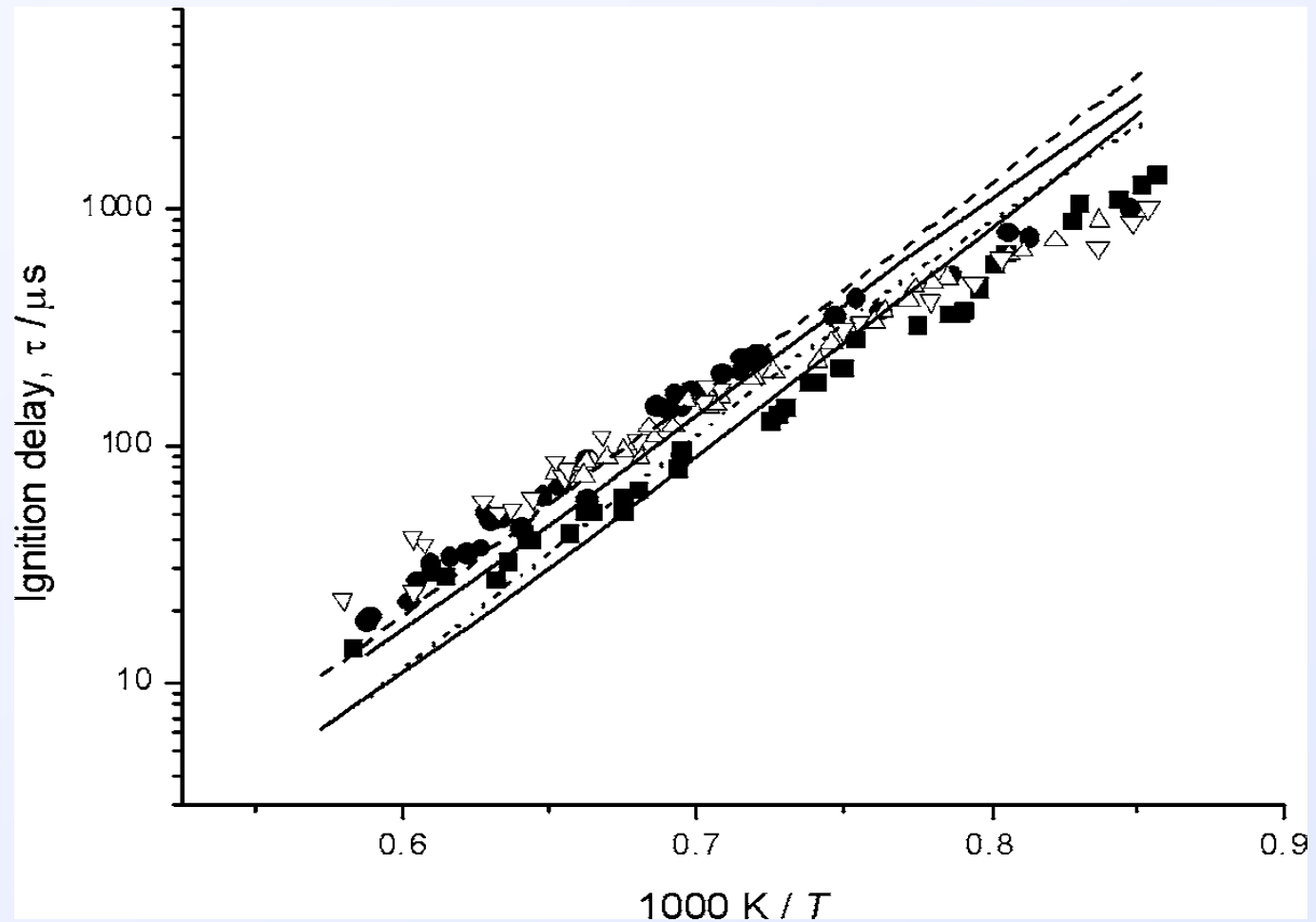
# Ignition of many saturated alkane fuels



Burcat et al. 1971, Westbrook et al. 2001

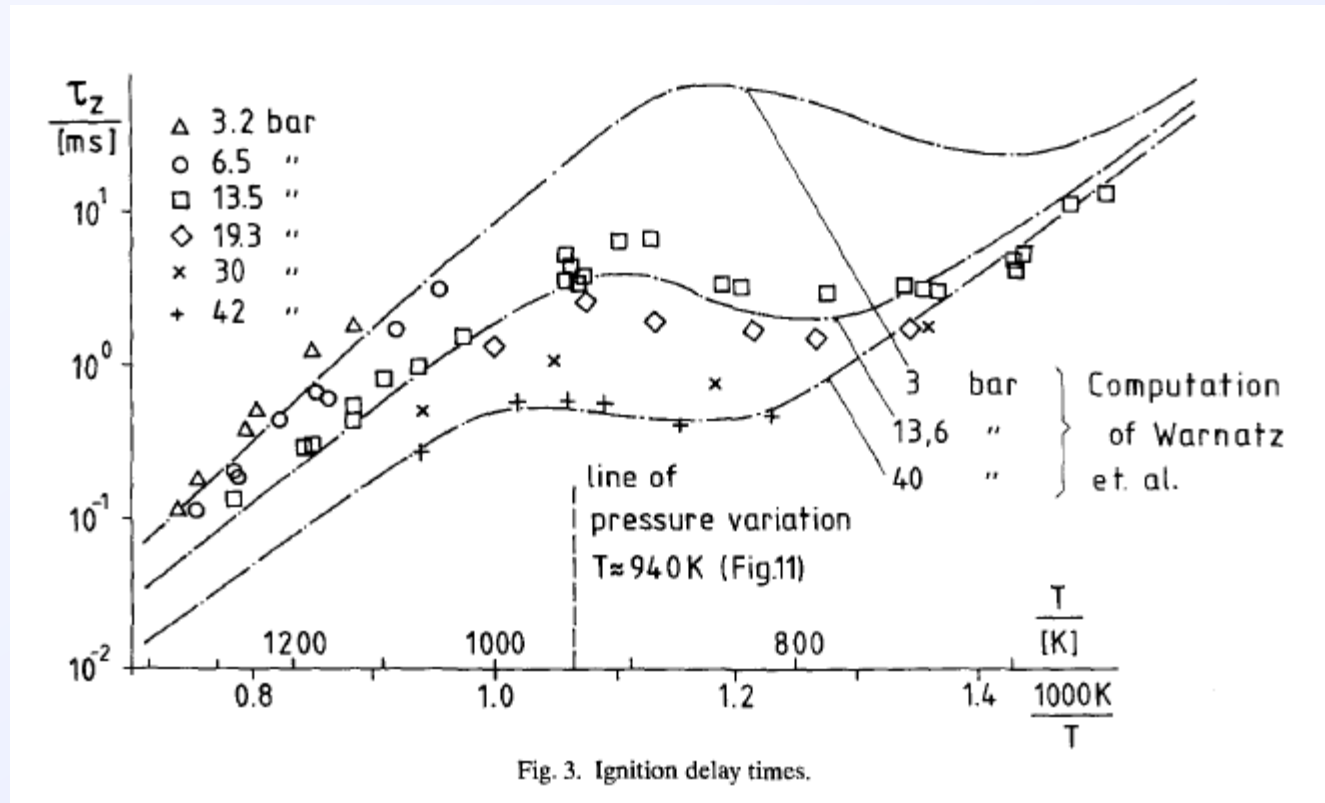
# High temperature ignition in shock tubes

Smith et al., IJCK 2005



**Figure 5** Heptane experimental (points) and model-predicted (lines) ignition delay times at 1.89% fuel,  $P_5 = 2.0 \pm 0.2$  atm, and  $\phi = 1.0$  in Ar: —■  $n$ -heptane, ···△ 2,3-dimethylpentane, —● 2,2-dimethylpentane, ---▽ 2,2,3-trimethylbutane.

# Shock tube results from Adomeit et al.



Fuel n-heptane Ciezki et al., 1993

# Moving to lower temperatures

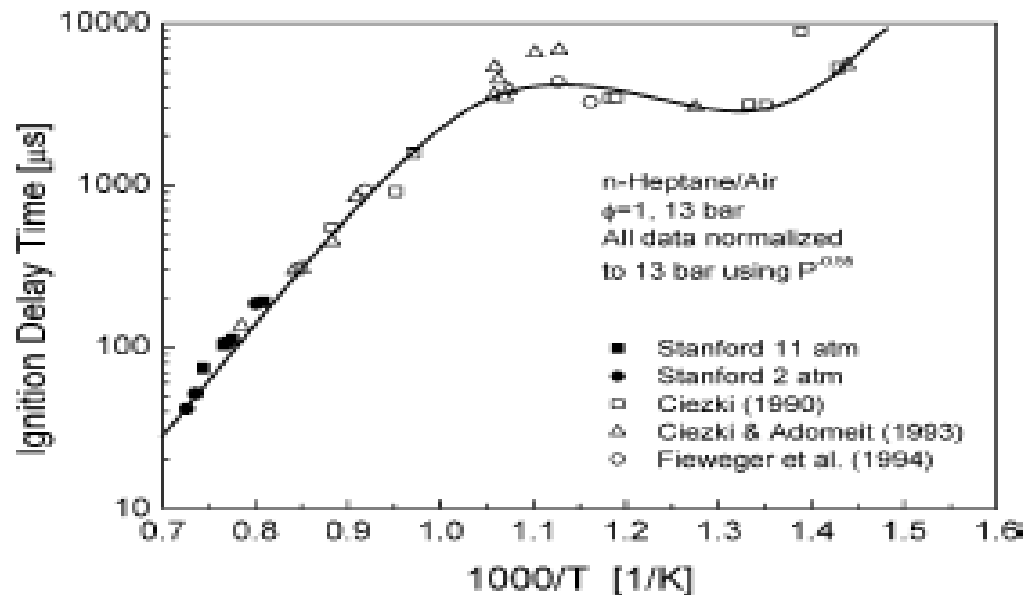


Fig. 10. *n*-Heptane/air ignition delay times for the low-pressure regime.  $\phi = 1.0$ .

Gautier et al. 2004

# Heptane isomers

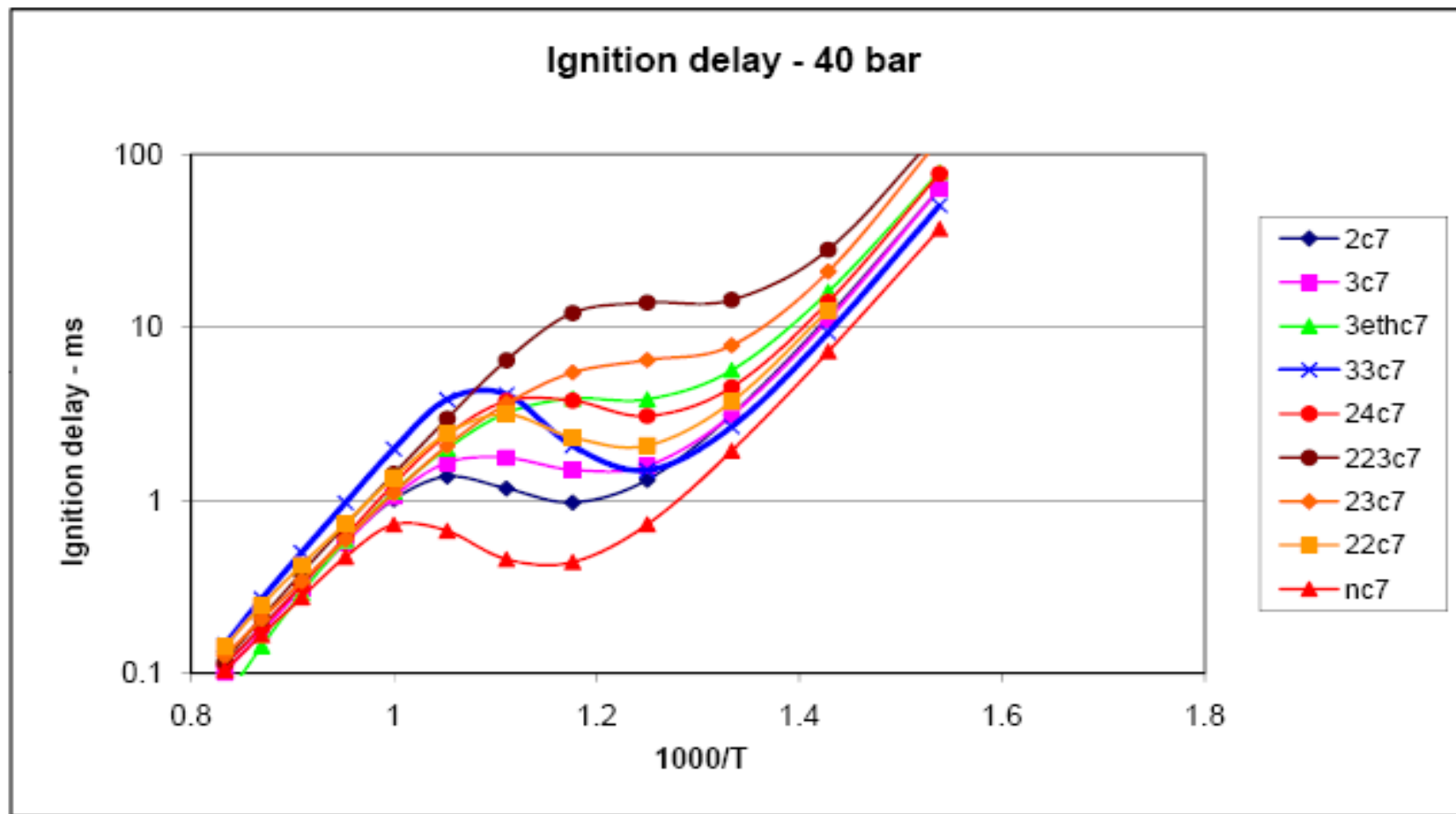
Octane numbers of heptanes are due exclusively to their different molecular structures

Low octane fuels have lots of secondary C-H bonds and high octane fuels have lots of primary C-H bonds and lots of tight, 5-membered TS Rings

2001/2002

C C C C C C C	RON 0
C C C C C C	42
C C C C C C	52
C C C C C C	93
C C C C C C	81
C C C C C C	83
C C C C C	91
C C C C C	65
C C C C	112

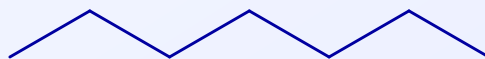
# Isomers of heptane – ignition delays



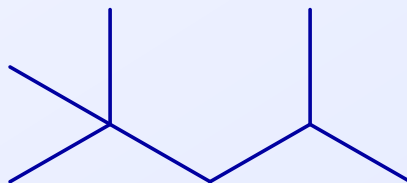
For a long time I thought we had done a lot of things correctly, but the results for 33c7 mean there are errors that need to be addressed. We now know there are additional errors

# Primary Reference Fuels for Gasoline

**n-heptane    Octane Number = 0**



**iso-octane    Octane Number = 100**

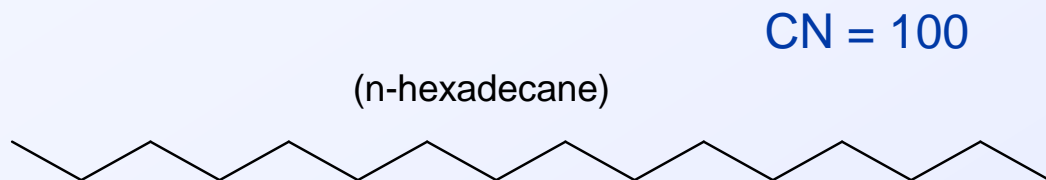




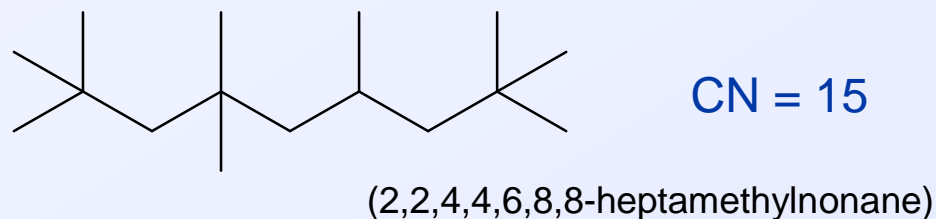
# We have assembled primary reference fuel mechanism for diesel fuel

- Diesel PRF:

- n-cetane



- iso-cetane

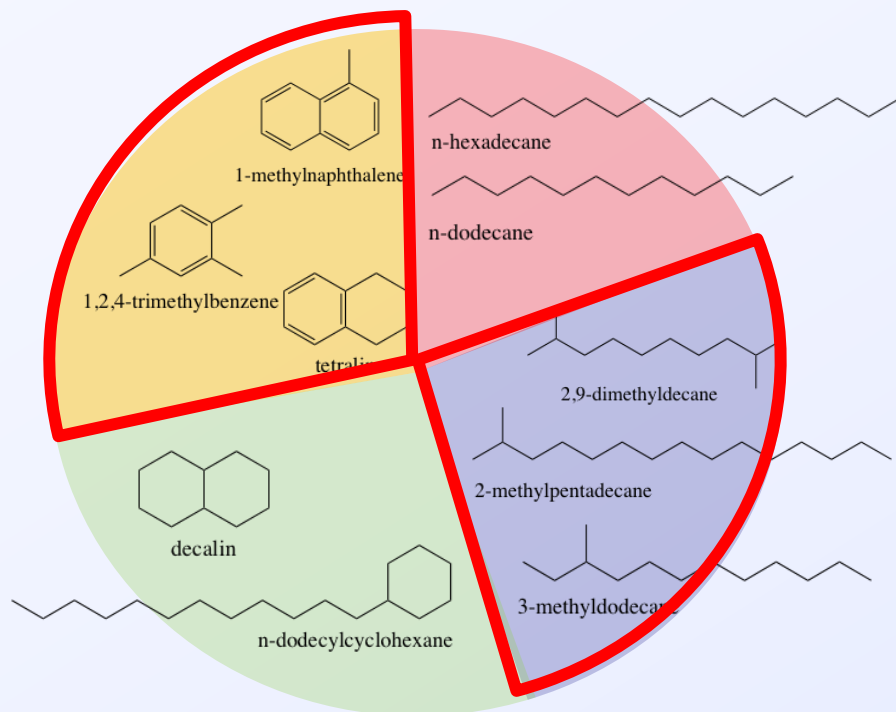


- PRF for Diesel mechanism:

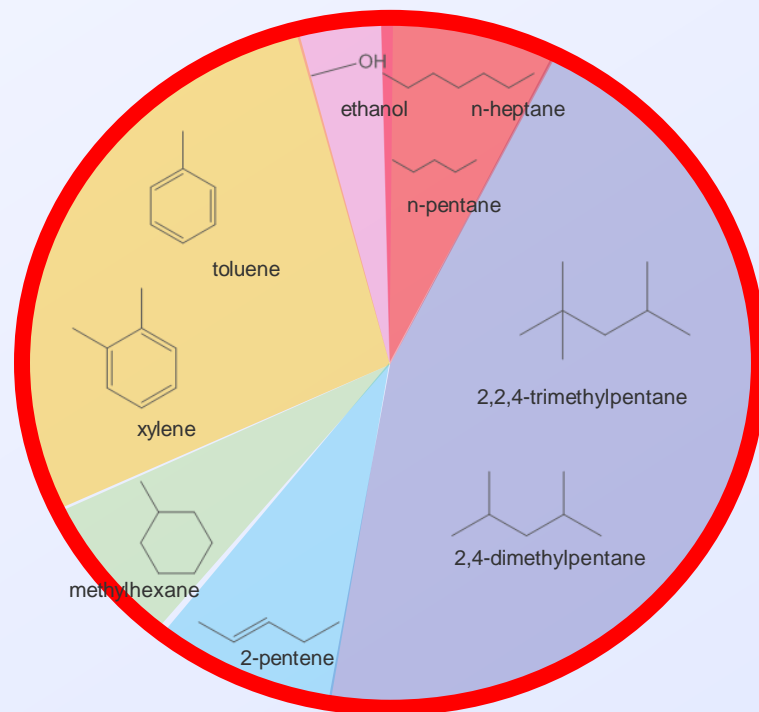
- 2,837 species
- 10,719 reactions

# Our fuel palettes

## Diesel fuels



## Gasoline fuels



■ n-alkanes

■ cycloalkanes

■ olefins

■ branched alkanes

■ aromatics

■ oxygenates

# Key reaction paths for alkanes

- Differences between C – H bond energies for primary sites and secondary sites
- Number of atoms in low temperature transition state rings involved in RO<sub>2</sub> isomerizations
- These factors used fundamental chemical principles to explain the sources of octane numbers in SI engines and cetane numbers in Diesel engines. These numbers had been recognized for 75 years but never based on basic chemical principles.

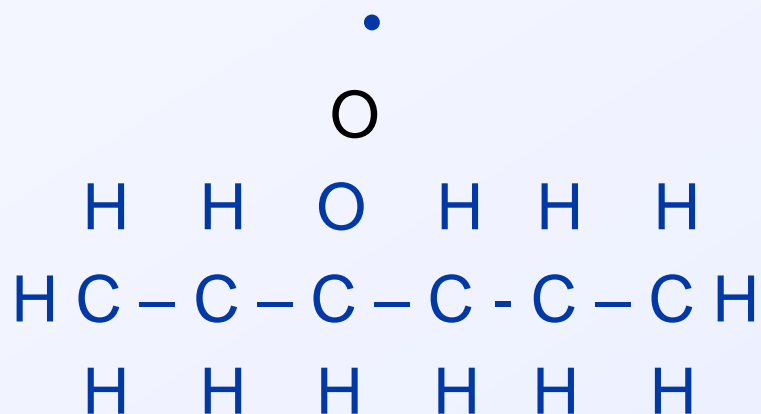
# Reactions of alkyl radicals and O<sub>2</sub>

- Mod 1.0 purely addition reactions with rapid stabilization
- Questions first arose from studies of C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> + HO<sub>2</sub> by Dean, Taatjes, Gutman/Slagle, Kaiser, Schaefer, Green, Miller/Klippenstein, etc., led to
- Recent work of Taatjes and Zador on molecular elimination pathways
- Recent work by Dean group on RO<sub>2</sub> and QOOH isomerizations
- NTC depends on accurate balance between chain branching and propagation pathways in low T regime – major opportunity?
- Importance of “rule-based” kinetic pathways
- This research system is working the way it is intended

# $R + O_2 = RO_2$ reaction is the gateway to LTO

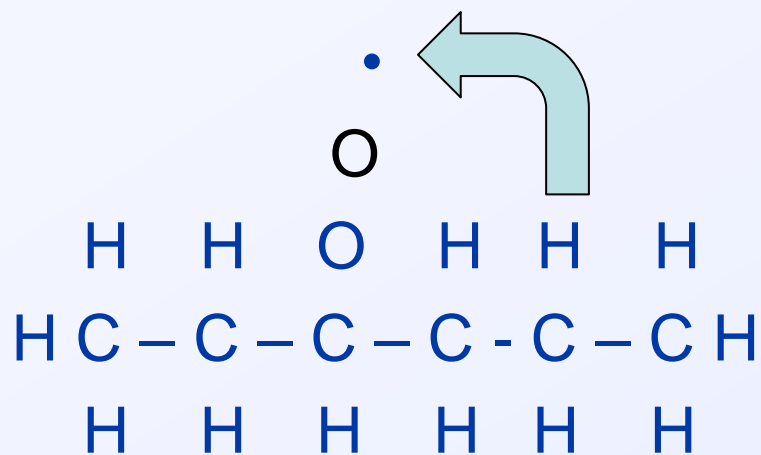
- Rising temperature leads to dissociation and ends all of the LTO kinetics
- $RO_2$  can be very unstable if  $O_2$  tries to attach to a weak bonding site
- Weak bonding sites can result from a wide range of structural chemistry reasons

## Class 12 – RO<sub>2</sub> isomerization

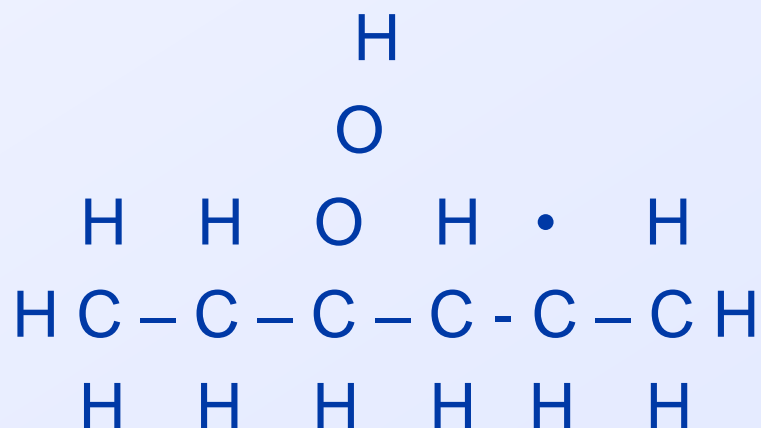
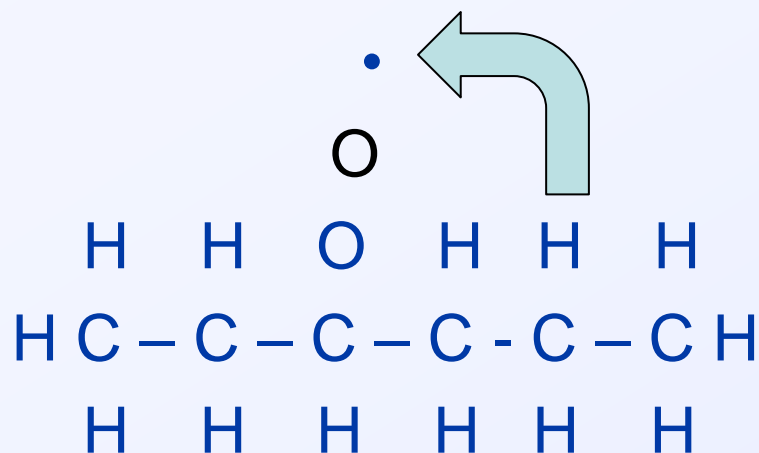


Transfer H atom within the molecule

## Class 12 – RO<sub>2</sub> isomerization

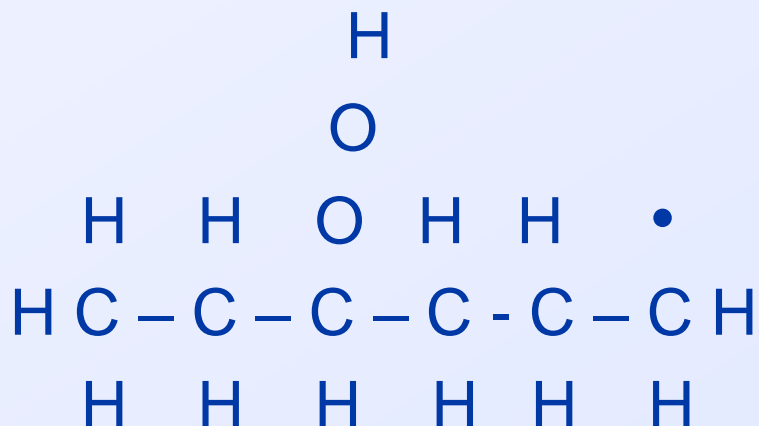
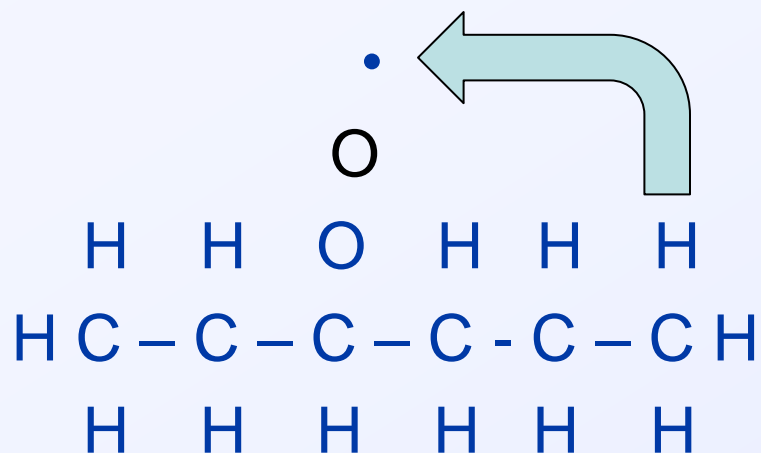


## Class 12 – RO<sub>2</sub> isomerization





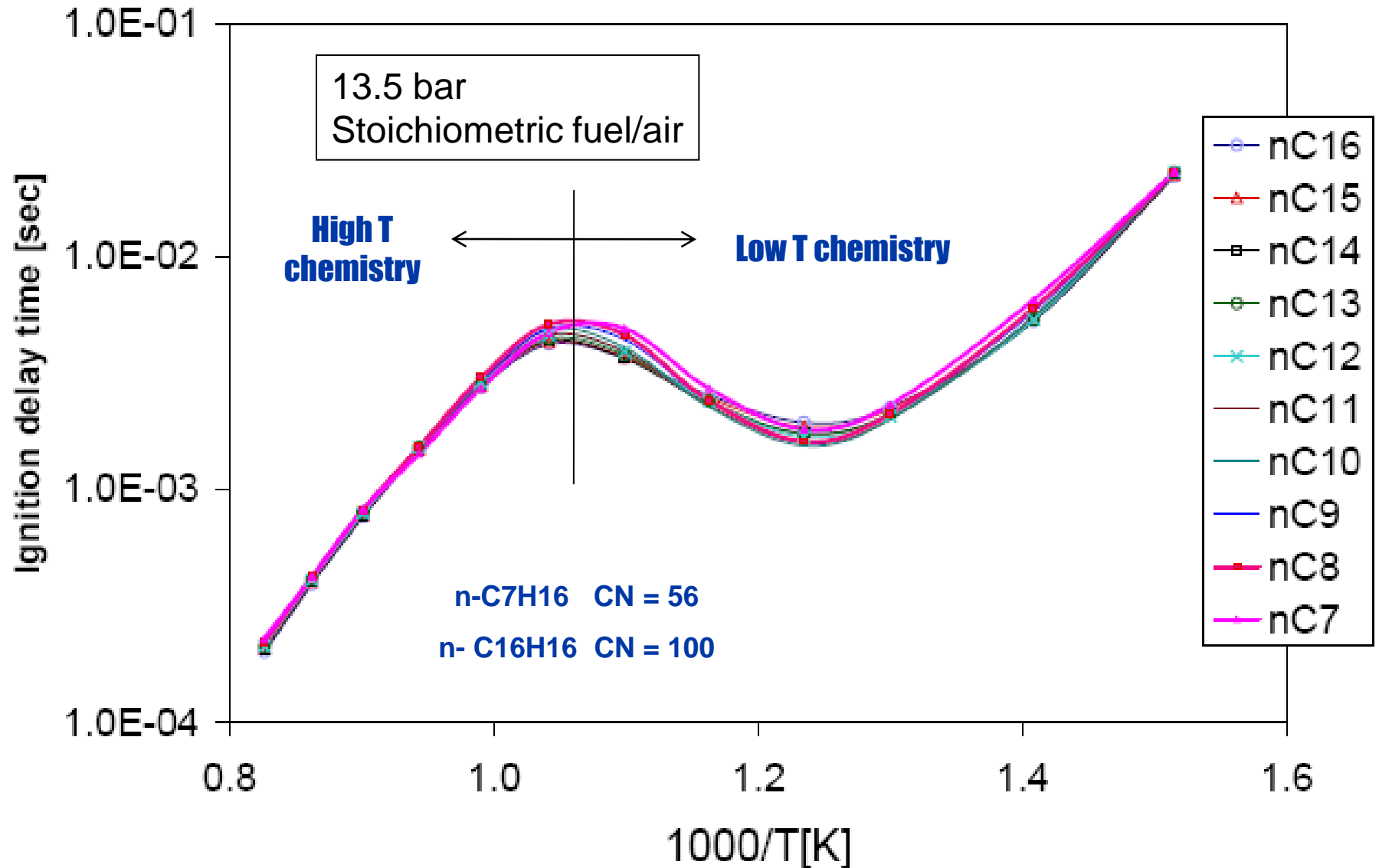
## Class 12 – RO<sub>2</sub> isomerization



# RO<sub>2</sub> isomerization reactions have many uncertainties

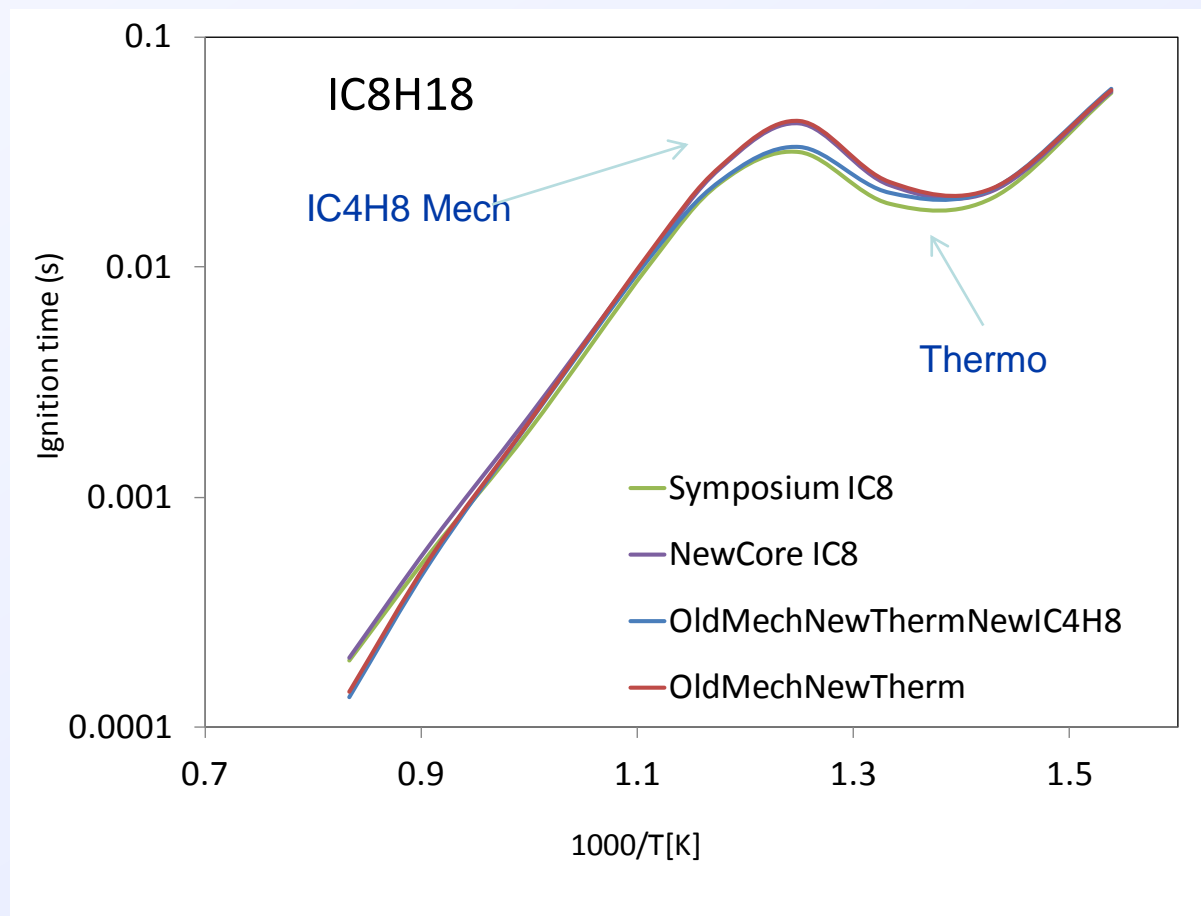
- These reactions were initially proposed to explain CN influences of C = C double bonds
- C = C double bonds inside transition state ring could affect rates of isomerization
- *cis* vs. *trans* structures can affect rates of these isomerization reactions
- New theory analysis may have resolved these issues, together with better thermochemistry of *bis*-allylic bonds

These results appear inconsistent with what we know about CN

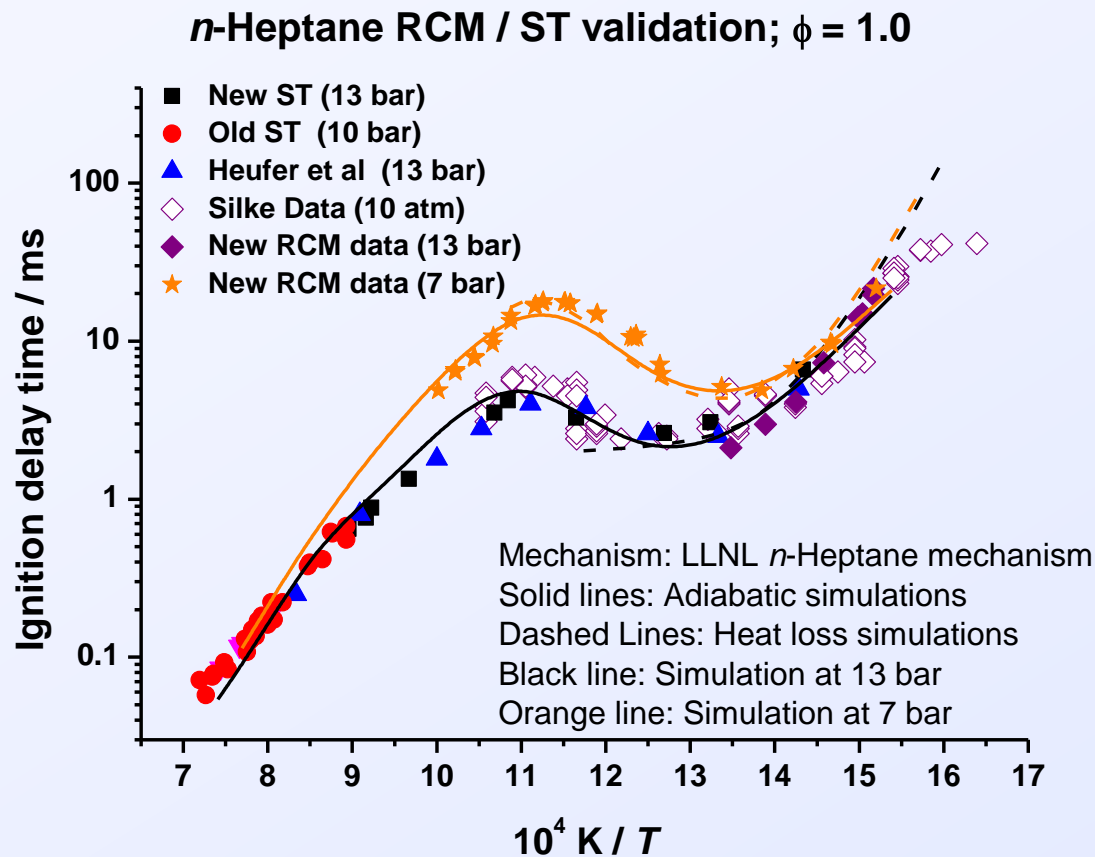


# Take a closer look at these curves

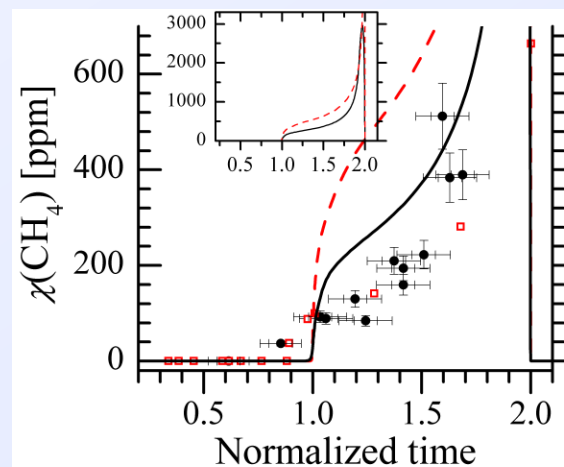
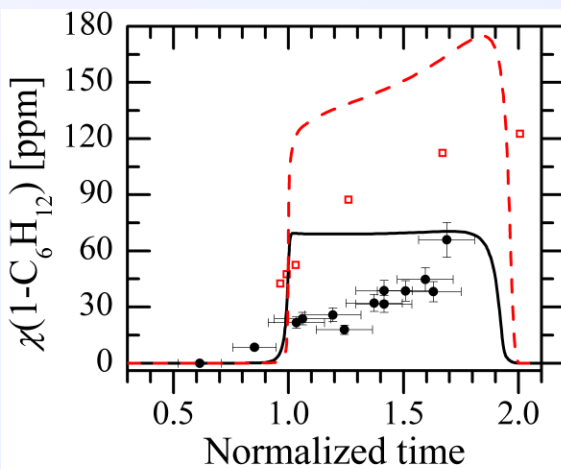
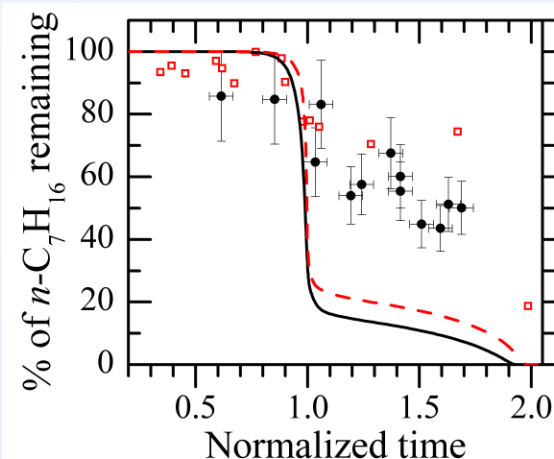
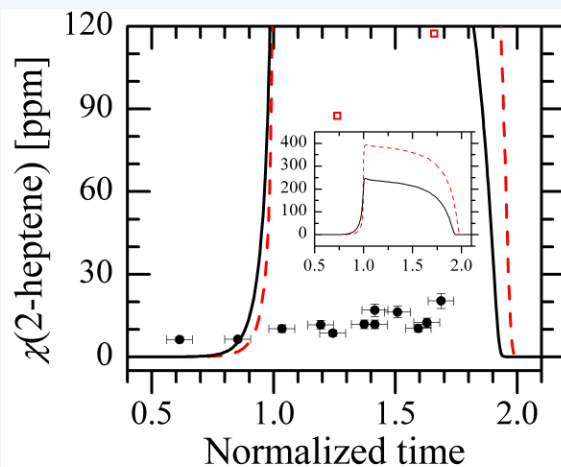
20 atm,  $\text{PHI}=1$



# These ignition curves have lots of structure



# Species measurements change the game



# More careful analysis showed some errors in n-alkane mechanisms

- Lumping of alkenyl radicals done incorrectly

in n-C<sub>8</sub>H<sub>18</sub> mechanism



in n-C<sub>12</sub>H<sub>26</sub> mechanism



Rate of  ${}_2\text{C}_8\text{H}_{16} + \text{R} = \text{RH} + {}_2\text{C}_8\text{H}_{15}$  equal to

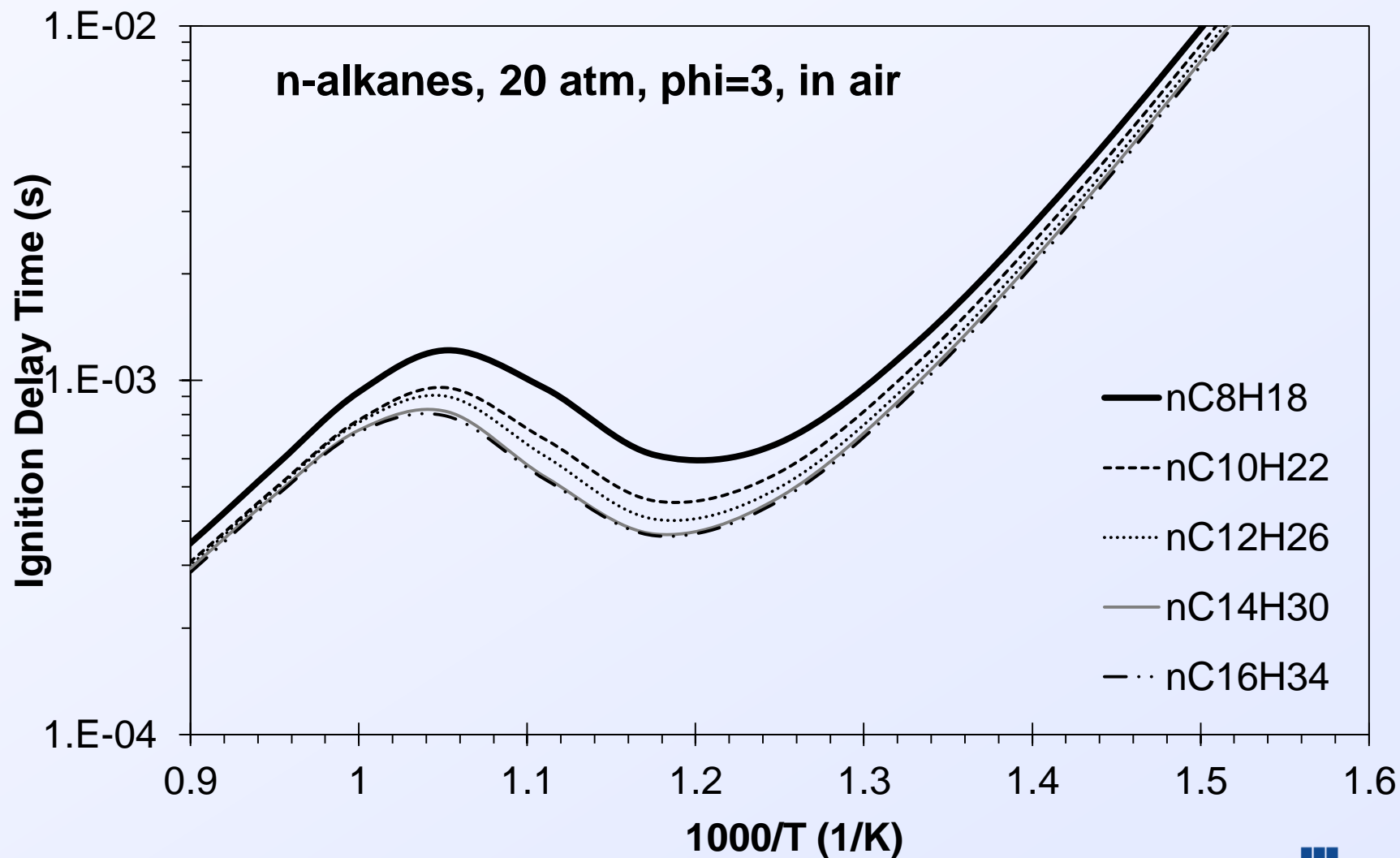
Rate of  ${}_2\text{C}_{12}\text{H}_{24} + \text{R} = \text{RH} + {}_2\text{C}_{12}\text{H}_{23}$

## Key - more complex questions are being asked

- Details of alkene reactions relatively unimportant if the only question is to predict the ignition delay or laminar burning velocity
- For me, the issue didn't arise until we became interested in biodiesel fuels, but it also affects kinetics of any hydrocarbon fuel with C=C double bonds, where the fuel itself is an olefin.
- Species-specific experiments are essential, recently there have been many more such experiments



## Similar calculations at higher equivalence ratio give different results

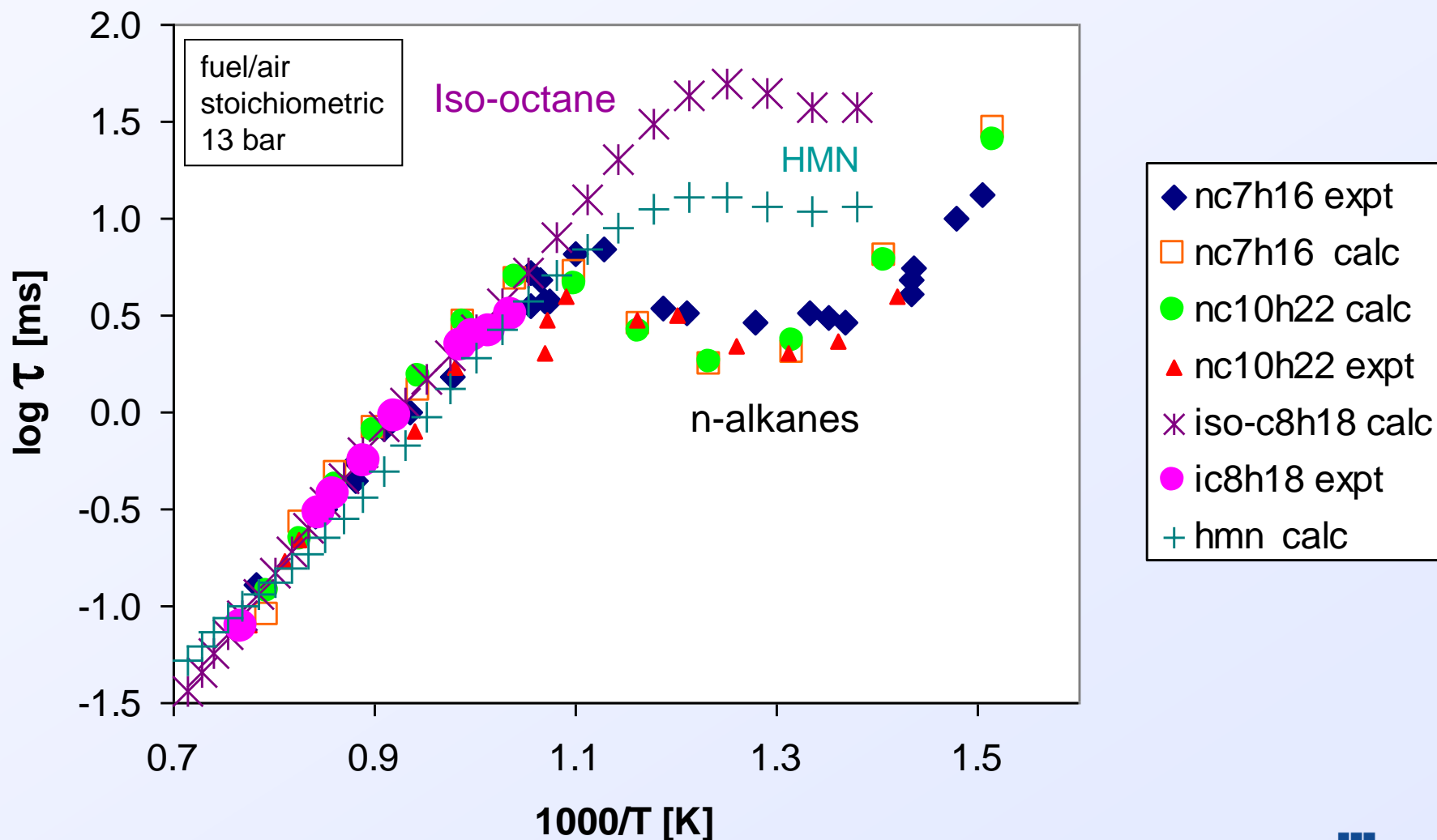
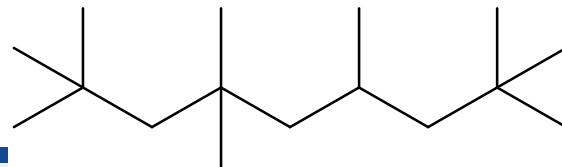


# This led us to use our kinetic models to look in depth at kinetics of CN

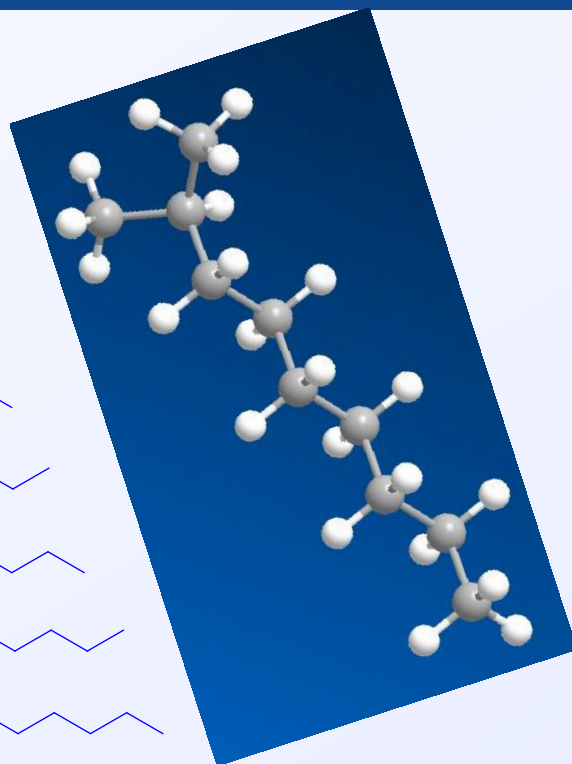
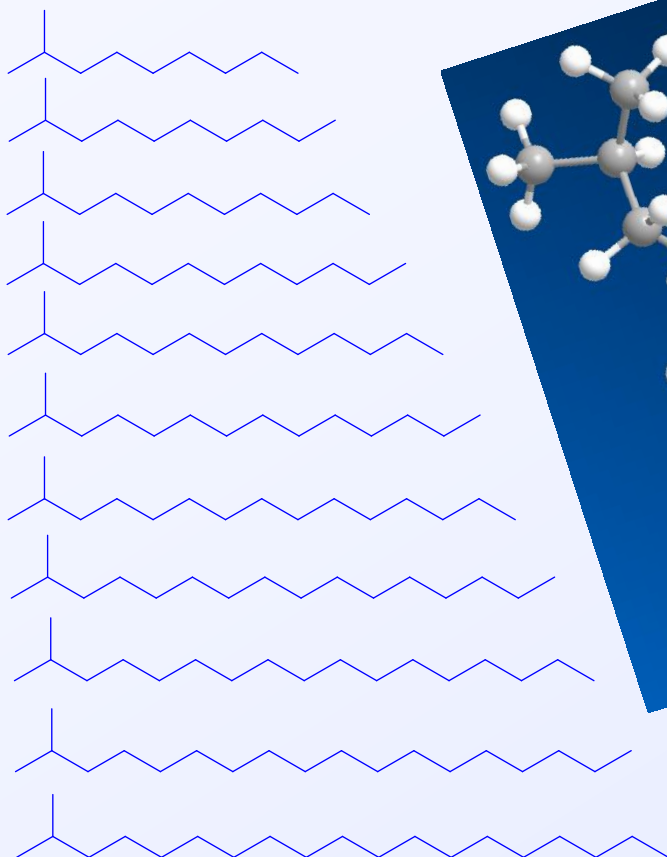
- Some reaction conditions and results don't depend on the size and structural features that influence CN
  - e.g.  $\phi = 1$ , 13 bar shock tube ignitions
- Try to find conditions where CN makes a difference but can be examined in idealized laboratory experiments
  - e.g. PSR, RCM and pressures and equivalence ratios
- Diesel ignition occurs for high pressure, fuel-rich conditions, so 13.5 bar and  $\phi = 1$  may be unrealistic
- At the same time, we want to understand what kinetic factors affect CN
- We now have more classes of mechanisms to use in these kinetic studies

# HMN ignition results at 13 bar:

2,2,4,4,6,8,8, heptamethylnonane



# Chemical Kinetic Mechanism for 2-methyl alkanes



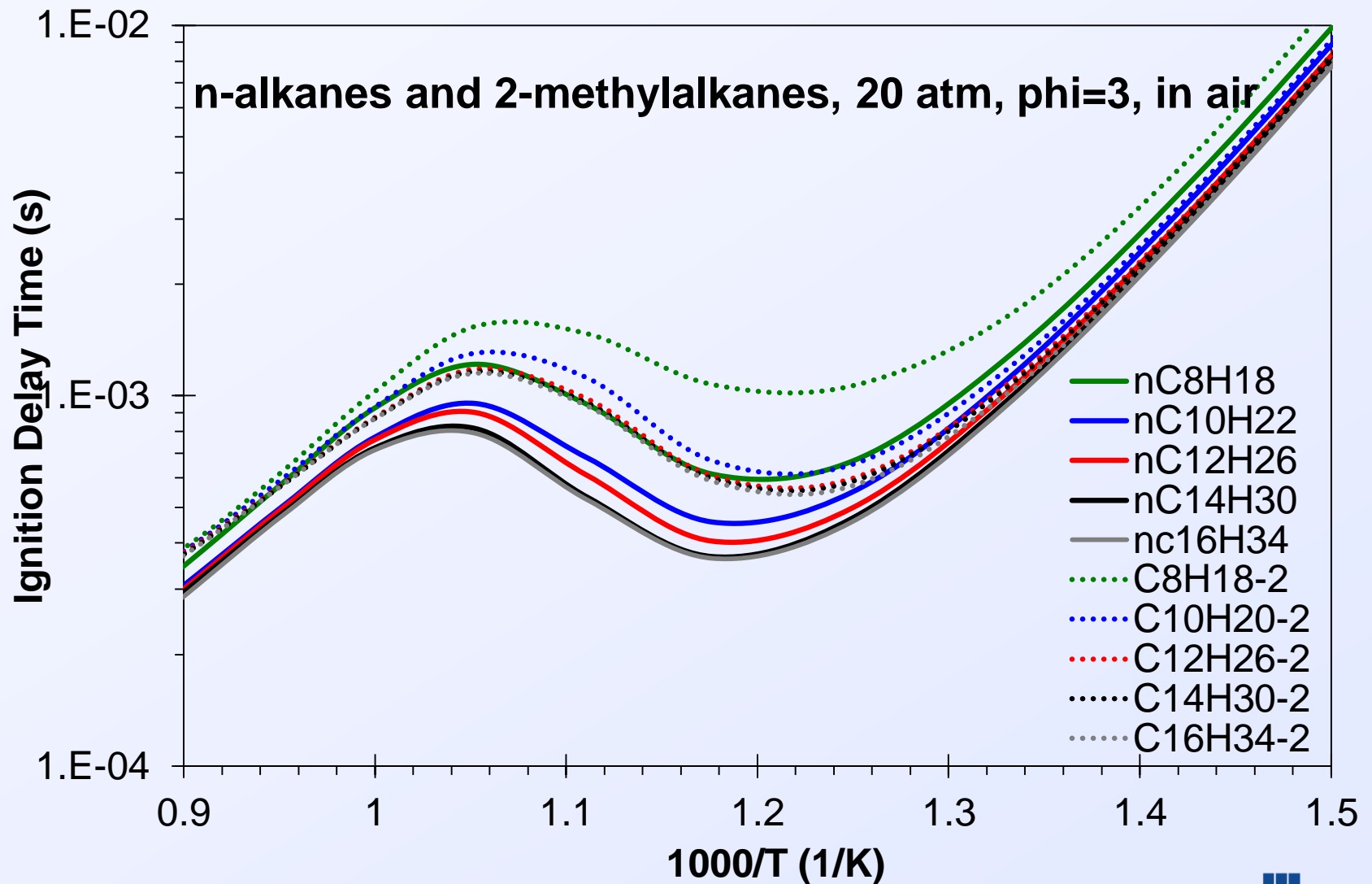
Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline, jet and diesel fuels

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms.

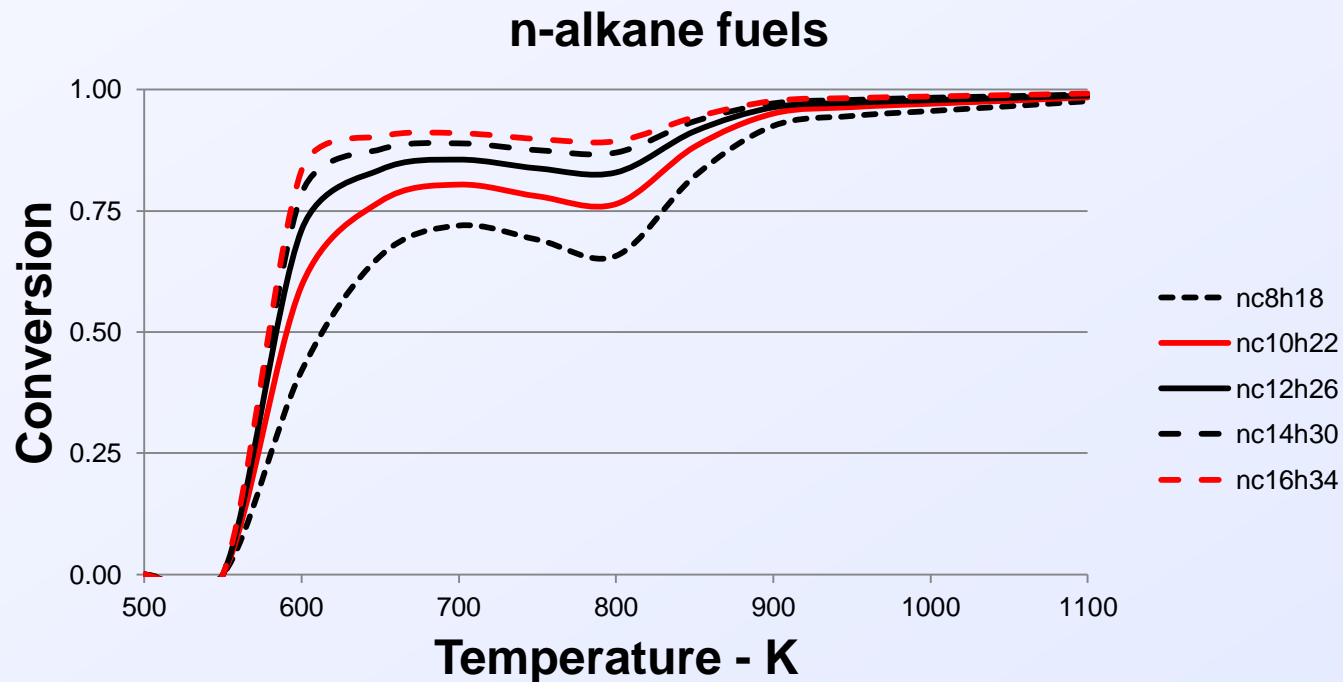
7,900 species  
27,000 reactions

Key fuel species to study Fischer-Tropsch fuels

# 2-methyl alkanes ignite slower than n-alkanes

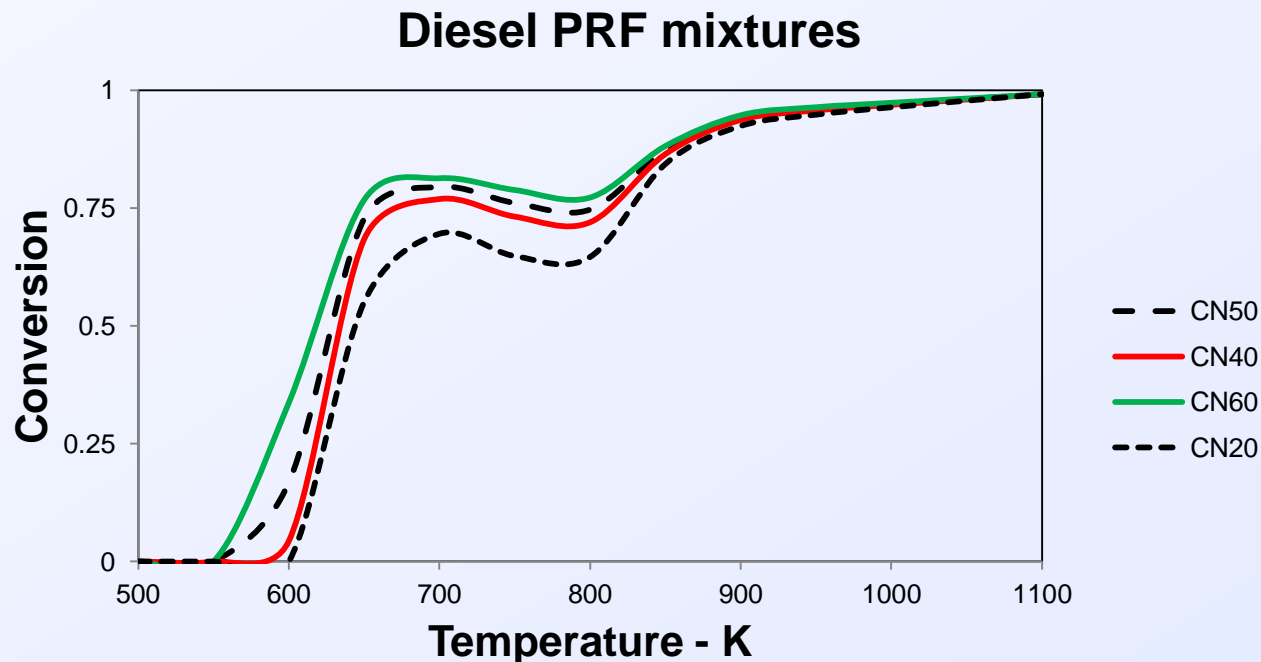


# PSR separates the n-alkanes by CN value



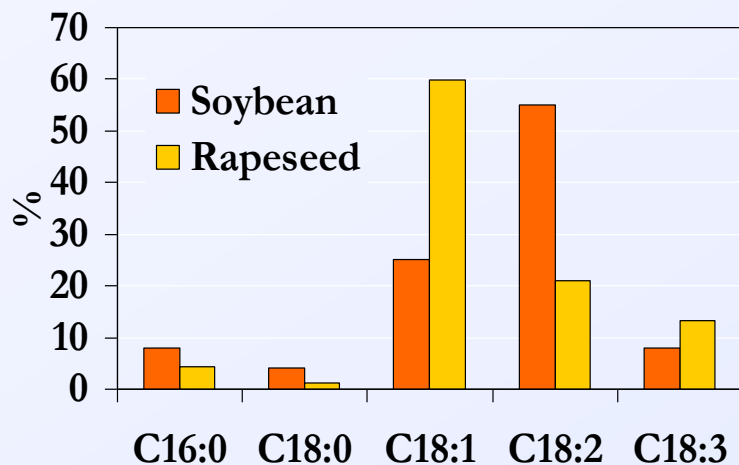
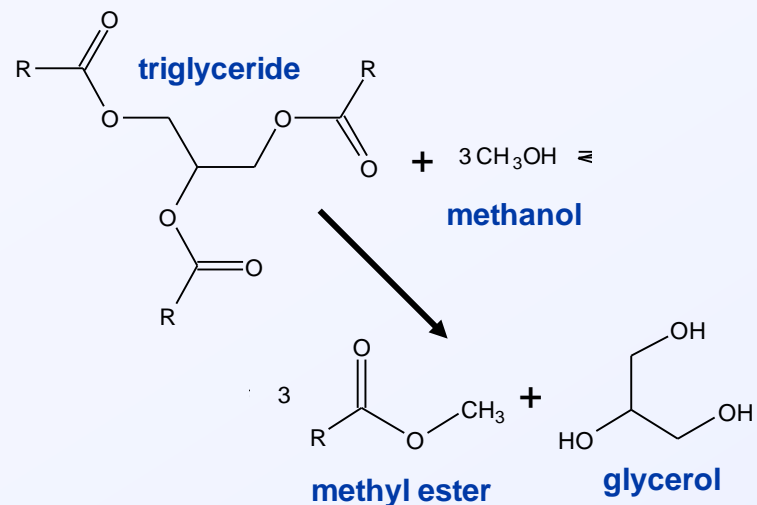
Fuel – rich ( $\phi = 3.0$ ) and high pressures (50 bar) conditions

## We use the PSR to spread out the reaction zone

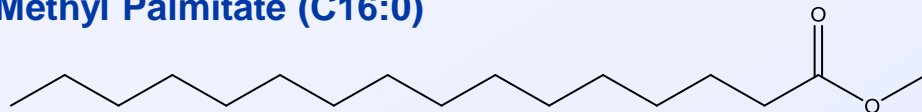


As CN increases, reaction in PSR starts at lower temperatures and has a greater extent of low T combustion

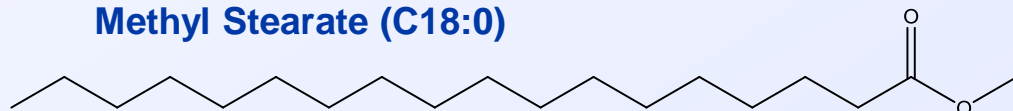
# Composition of Biodiesels



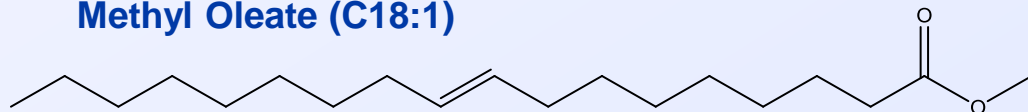
**Methyl Palmitate (C16:0)**



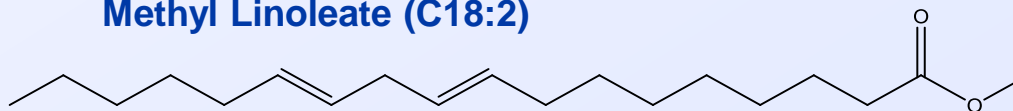
**Methyl Stearate (C18:0)**



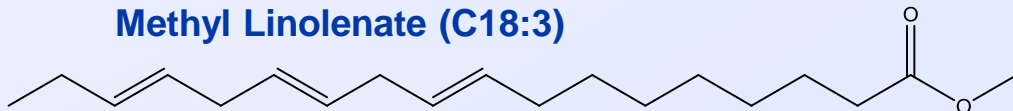
**Methyl Oleate (C18:1)**



**Methyl Linoleate (C18:2)**



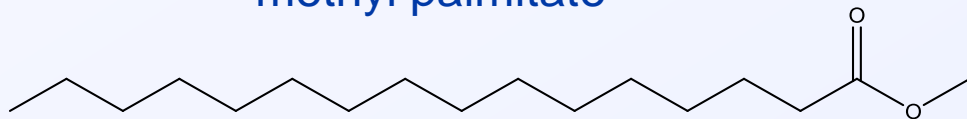
**Methyl Linolenate (C18:3)**



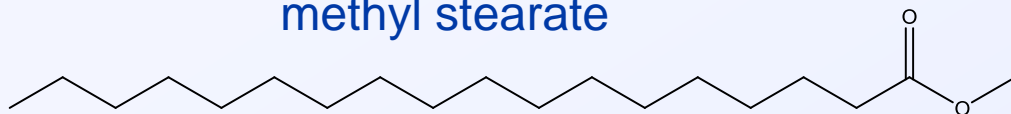


# Assembled chemical kinetic model for all of the remaining five main components in biodiesel derived from soybeans or rapeseed oil

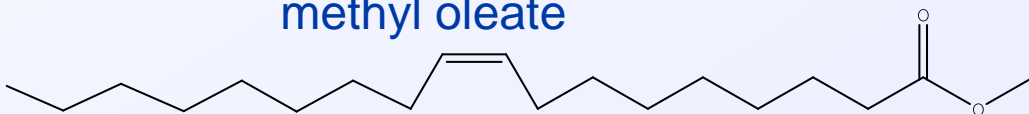
methyl palmitate



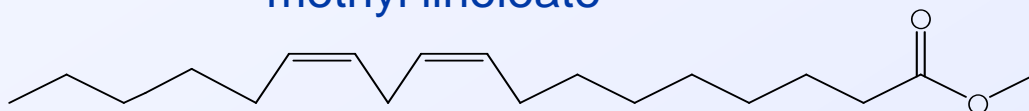
methyl stearate



methyl oleate



methyl linoleate



methyl linolenate



Built with the same reaction rate rules as our successful methyl decanoate and methyl decenoate mechanism

5 component mechanism, approximately

5,000 species  
20,000 reactions

Model with all 5 components now published and available:

Westbrook, Naik, Herbinet, Pitz, Mehl, Sarathy and Curran, "Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels," Combustion and Flame, 2011.



# Cetane numbers of biodiesel components

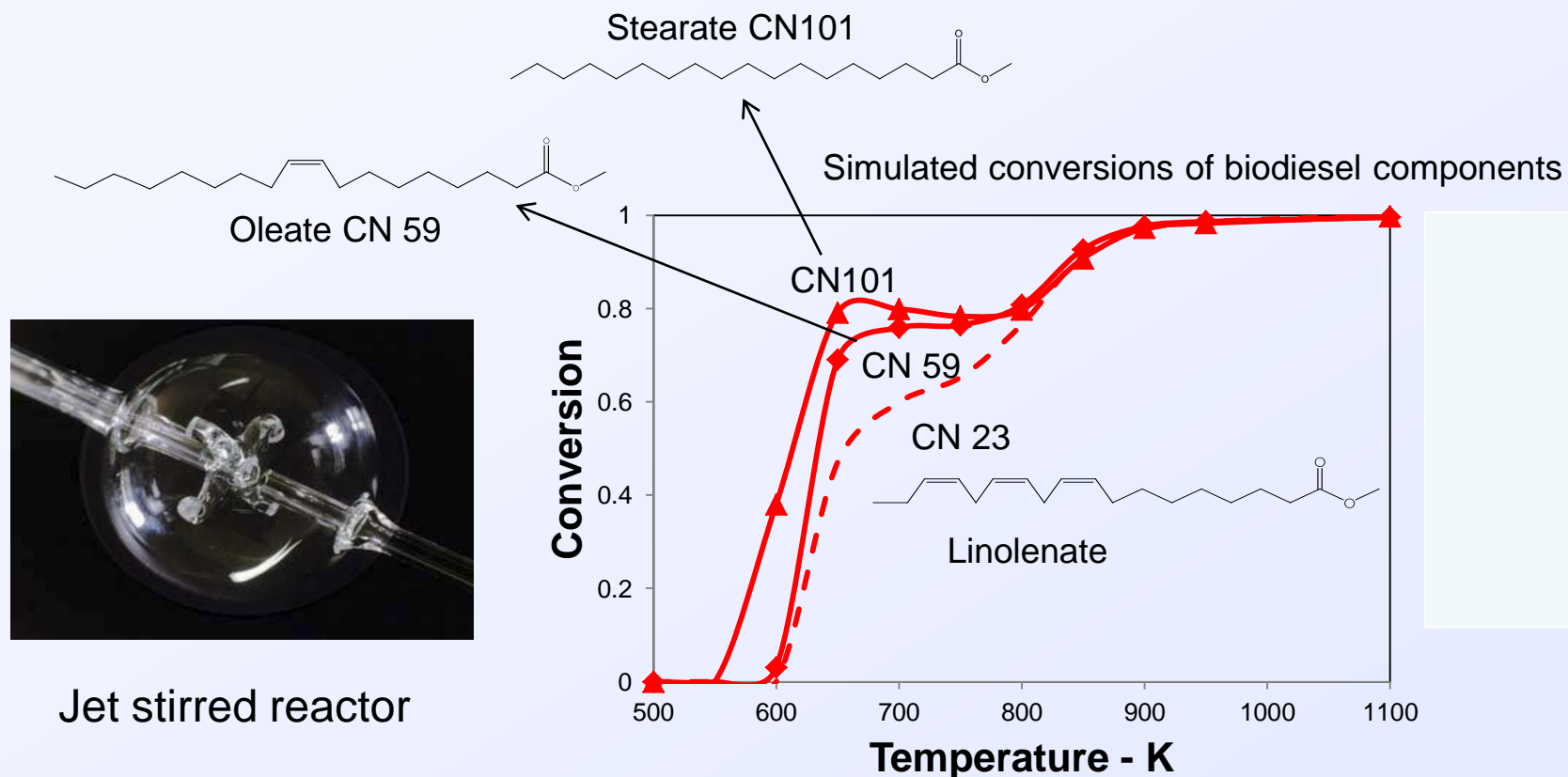
- Methyl stearate C18:0 CN = 101
- Methyl oleate C18:1 CN = 59
- Methyl linoleate C18:2 CN = 38
- Methyl linolenate C18:3 CN = 23
- Methyl palmitate C16:0 CN = 86

Number of C = C double bonds strongly affects CN

Chain length strongly affects CN

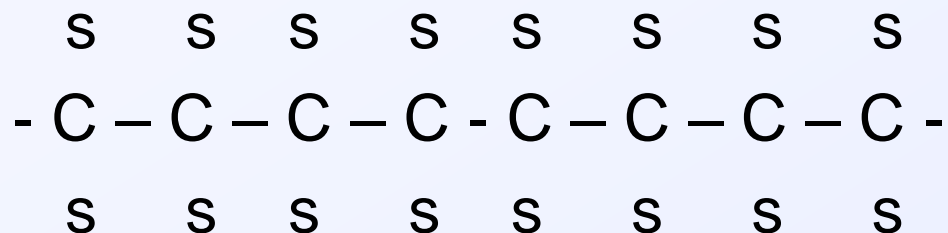
# Increased number of double bonds reduces low T reactivity of individual components in stirred reactor at diesel conditions

Diesel engine conditions of high pressure and fuel-rich mixtures:  
50 bar,  $\Phi=2$  (Fuel: 200 ppm, residence time = 0.05 s)



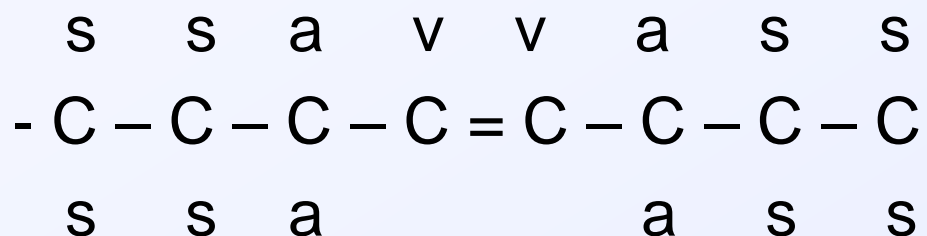
Derived cetane numbers from Knothe (2010)

# Effects of C = C double bonds in long chain molecules



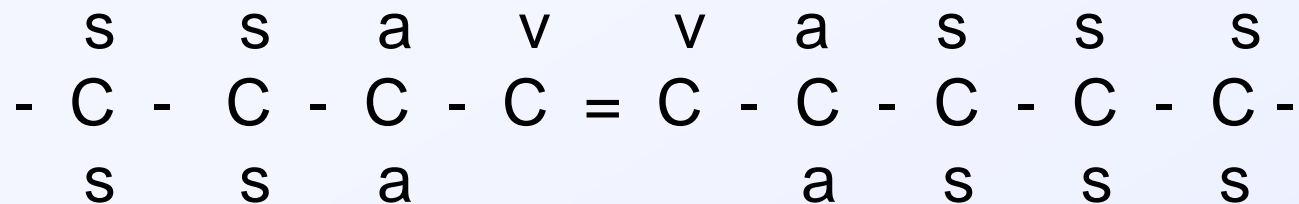
With no C = C double bonds, all CH<sub>2</sub> groups in the chain have the same C – H (and C – O O) bond strengths

# C = C double bonds reduce low T reactivity

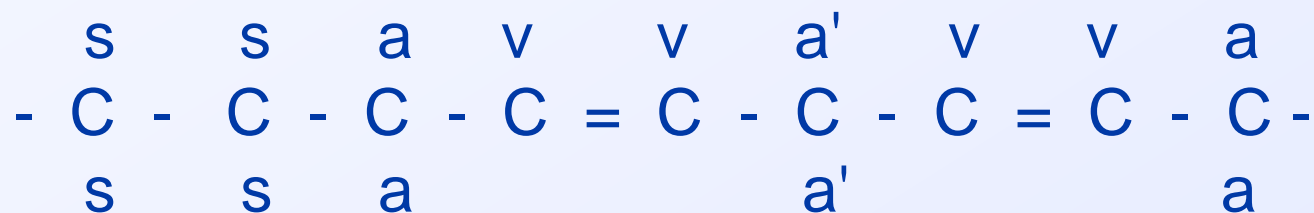
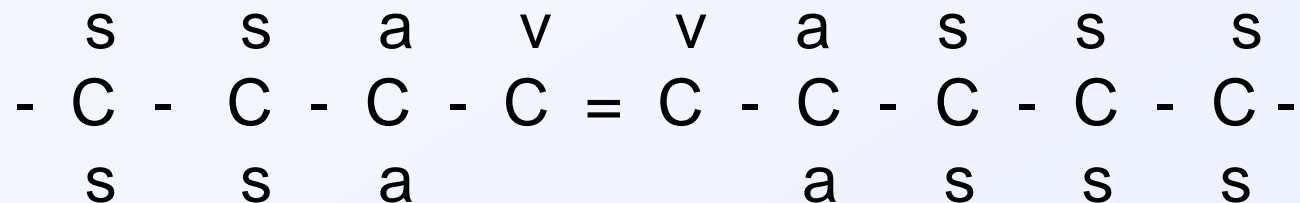


- Inserting one C=C double bond changes the C-H bond strength for 6 H atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O<sub>2</sub> is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

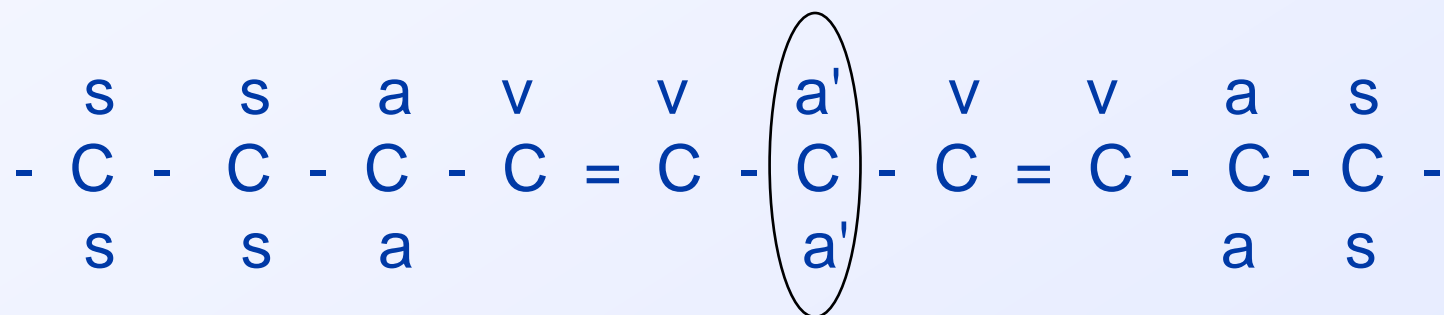
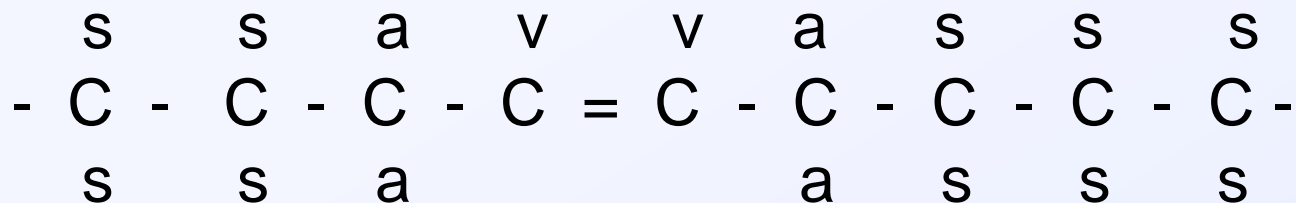
## Two double bonds make a huge difference



## Two double bonds make a huge difference



## Two double bonds make a huge difference



$\text{C} - \text{H} \quad \underline{\text{s}} \text{ bond} > \text{C} - \text{H} \quad \underline{\text{a}} \text{ bond} > \text{C} - \text{H} \quad \underline{\text{a}'} \text{ bond}$

Same trend with C – OO bonds

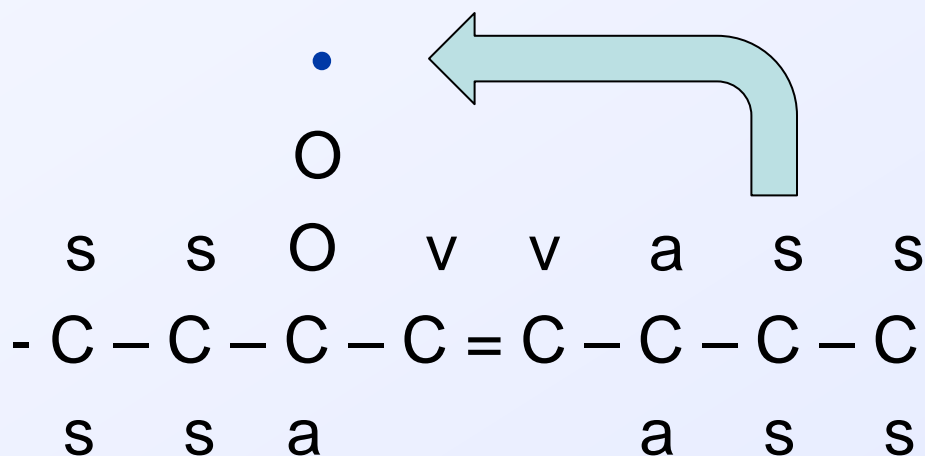


# Kinetic factors involved

- Equilibrium of  $R + O_2 + M = RO_2 + M$  additions  
Particularly weak bond at allylic sites
- Some authors have reported that transition state rings for  $RO_2$  isomerizations at low temperatures are strongly inhibited if there is a double bond in the transition state ring.
- We need theory analysis to examine these and other related factors

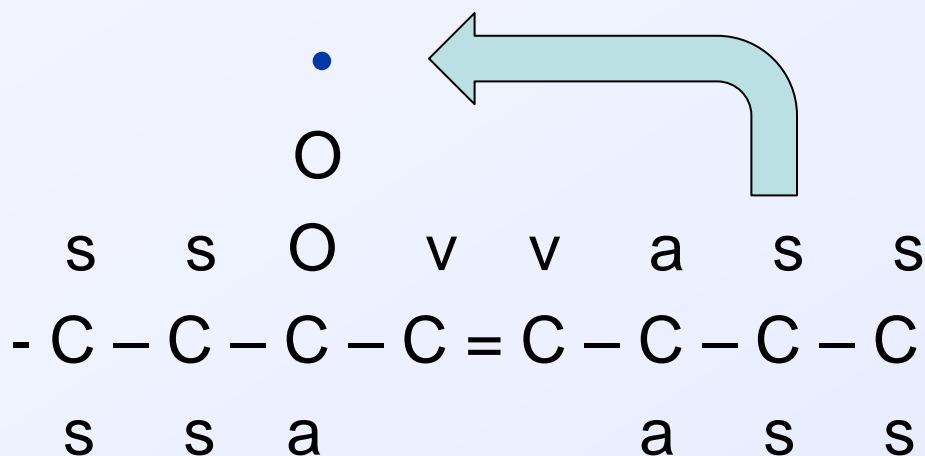
# C = C double bonds reduce low T reactivity

Does the C=C double bond change the rate of isomerization ?



# C = C double bonds reduce low T reactivity

Does the C=C double bond change the rate of isomerization ?



Probably not very much

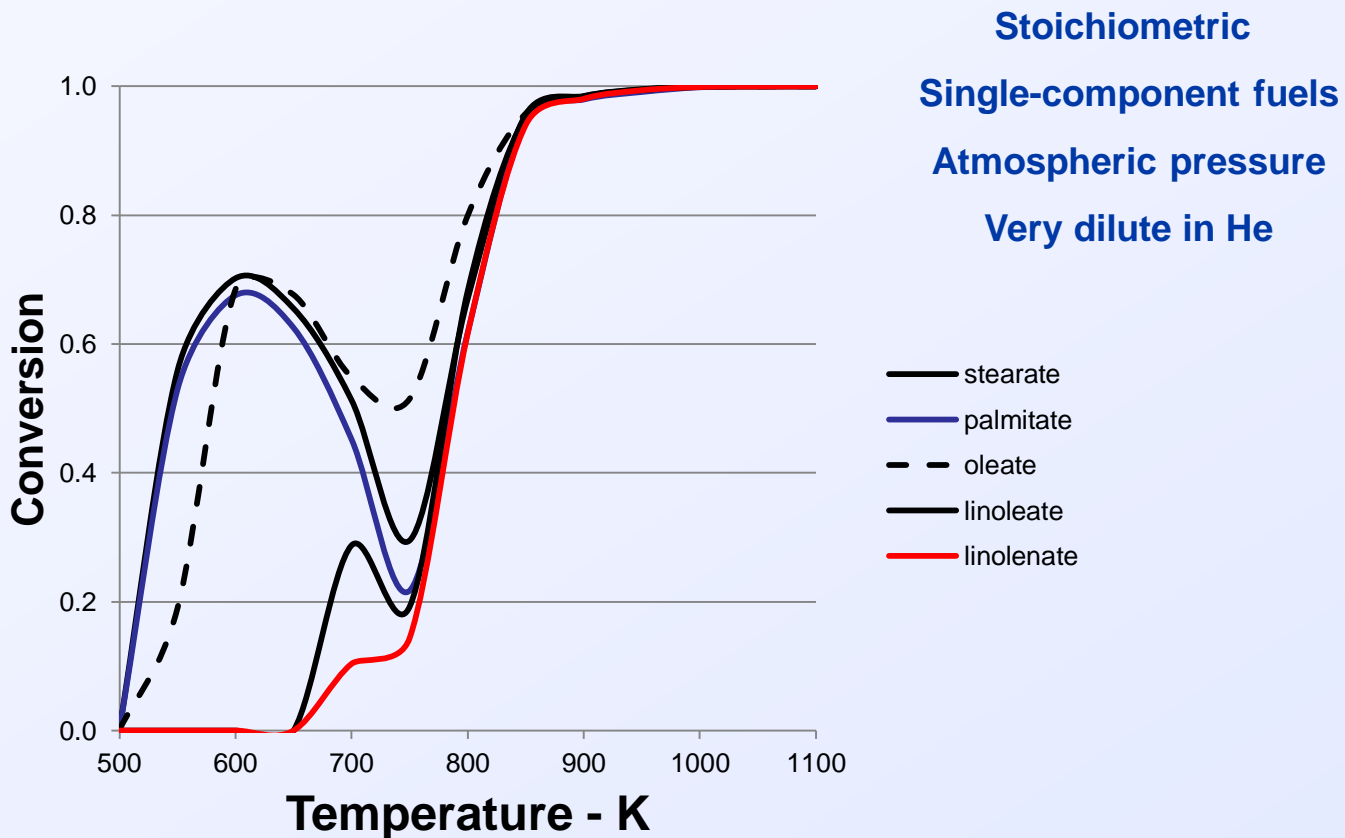
# Methyl linoleate has three C=C double bonds, one pair of allylic, weak C-H bonds and two very weak, *bis*-allylic CH<sub>2</sub> locations

The low bis-allylic bond strengths are also responsible for poor fuel stability of many of these fuels with 2 or 3 C=C double bonds

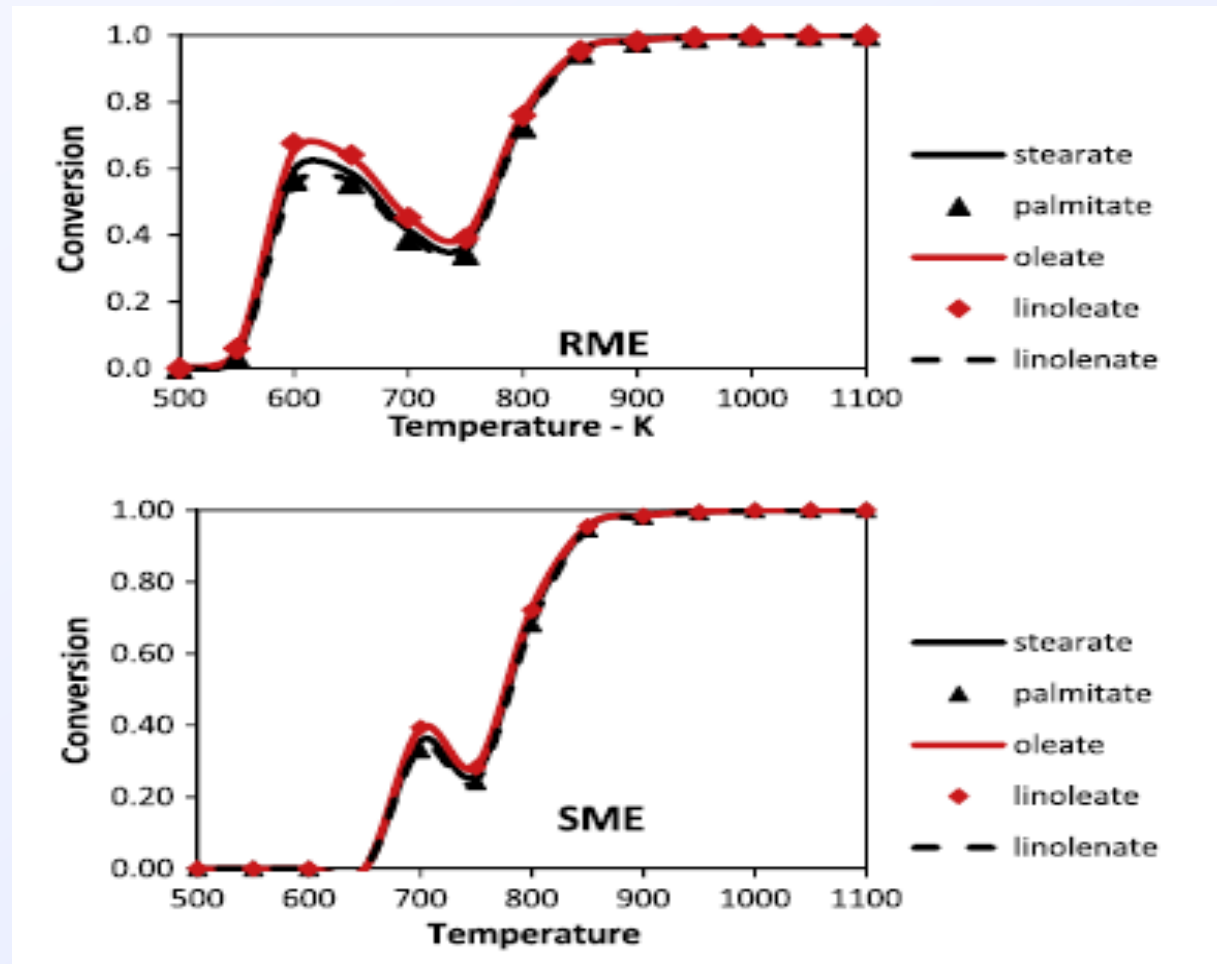
Some cell biology research is trying to increase oleate and decrease stearate, linoleate and linolenate in soy biodiesel fuel

14-Jun	mod9d12d15d	ro2	DeltaH
m	-47.15	-88.2	-41.05
2	-51.94	-83.04	-31.1
3	-47.65	-85.26	-37.61
4	-47.65	-85.26	-37.61
5	-47.65	-85.26	-37.61
6	-47.65	-85.26	-37.61
7	-47.65	-85.26	-37.61
8	-58.4	-85.35	-26.95
9	-37.1	-82.06	-44.96
10	-37.1	-82.06	-44.96
11	-70.11	-86.49	-16.38
12	-37.1	-82.06	-44.96
13	-37.1	-82.06	-44.96
14	-70.11	-86.49	-16.38
15	-37.1	-82.06	-44.96
16	-37.1	-82.06	-44.96
17	-58.4	-85.35	-26.95
18	-45	-81.8	-36.8

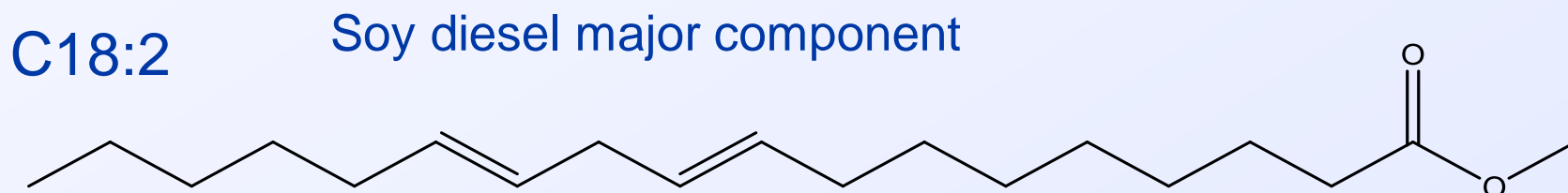
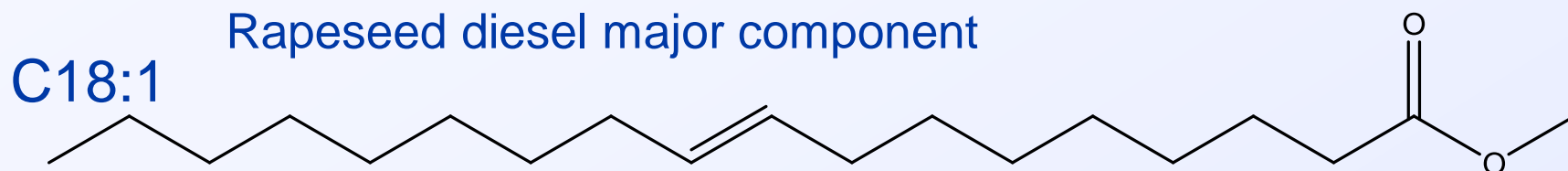
# Biodiesel components reactivities in JSR



# Soy and rapeseed biodiesel fuels in JSR



# Differences between soy and rapeseed fuels



Rapeseed CN = 54      Soy CN = 47

Double bonds in the carbon chain inhibit low T chemistry

# Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

	Sunflower	Safflower	Linseed	Jatropha	Cottonseed	Corn	Olive	beef tallow	Palm	Peanut	Soy	rapeseed
palmitate	7	7	7	4	23	10	13	28	46	11	8	4
stearate	5	2	1	8	3	4	4	21	4	8	4	1
oleate	19	13	19	49	20	38	72	47	40	49	25	60
linoleate	68	78	19	38	53	48	10	3	10	32	55	21
linolenate	1	0	54	1	1	0	1	1	0	0	8	14
CN	49	50	39	58	51	49	55	58	62	54	47	54

With models for all 5 major components, we can now model all these types of biodiesel:

- Not a surrogate model, but a real biodiesel (B100) model !



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# Biodiesel fuels from different oils

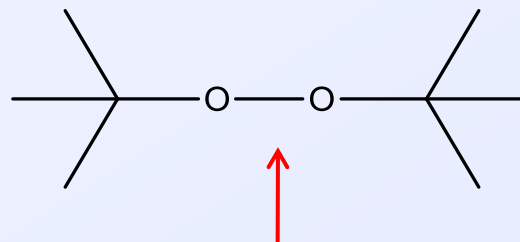
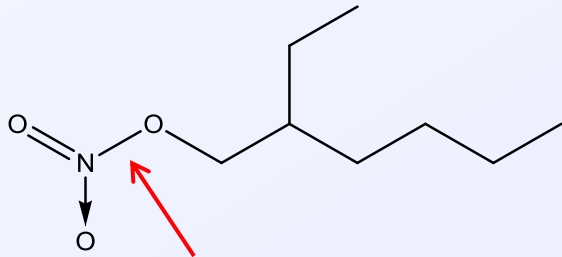
- Methyl ester fuels from different plant and animal fats and oils have different CN values
- Detailed composition of these biodiesel fuels determine their CN values
- Biggest factor for CN variability of biodiesel, large methyl ester fuels is the number of C=C double bonds
- We can model kinetics of most of these biodiesel fuels using the new biodiesel kinetic mechanism
- The mechanisms still need refinements and testing, and careful laboratory experiments would be very valuable

# Additives are used to increase CN

- Blending higher CN components
- We developed kinetic reaction mechanisms recently for ethyl hexyl nitrate and di-tertiary butyl peroxide
- For both additives, there is one very weak bond that is broken at quite low temperatures, producing very early heat release and promoting ignition

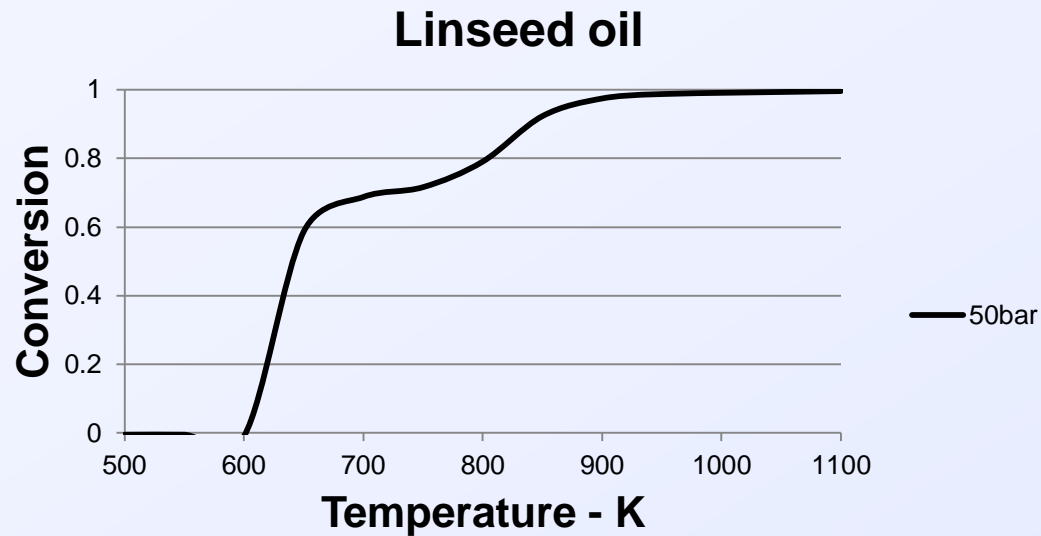
# Additives are used to increase CN

- Add additives to biodiesels with low CN (e.g. linseed derived biodiesel)
- We developed kinetic reaction mechanisms recently for ethyl hexyl nitrate (ENH) and di-tertiary butyl peroxide (DTBP)



- For both additives, there is one very weak bond that is broken at quite low temperatures, producing very early heat release and promoting ignition

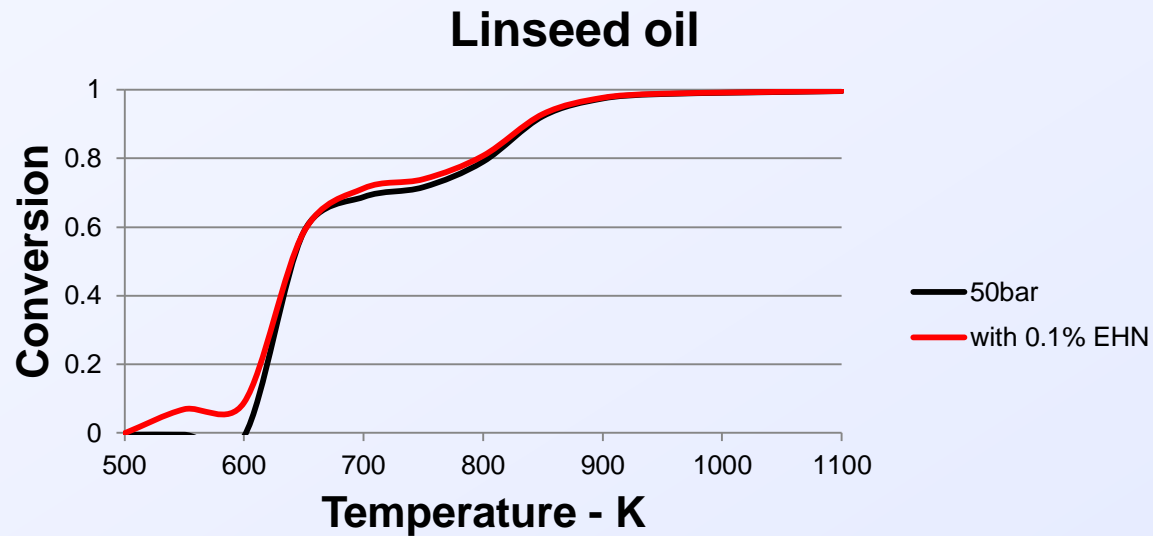
# Biodiesel fuel with lowest CN is linseed biodiesel



Linseed oil methyl ester fuel has CN = 39

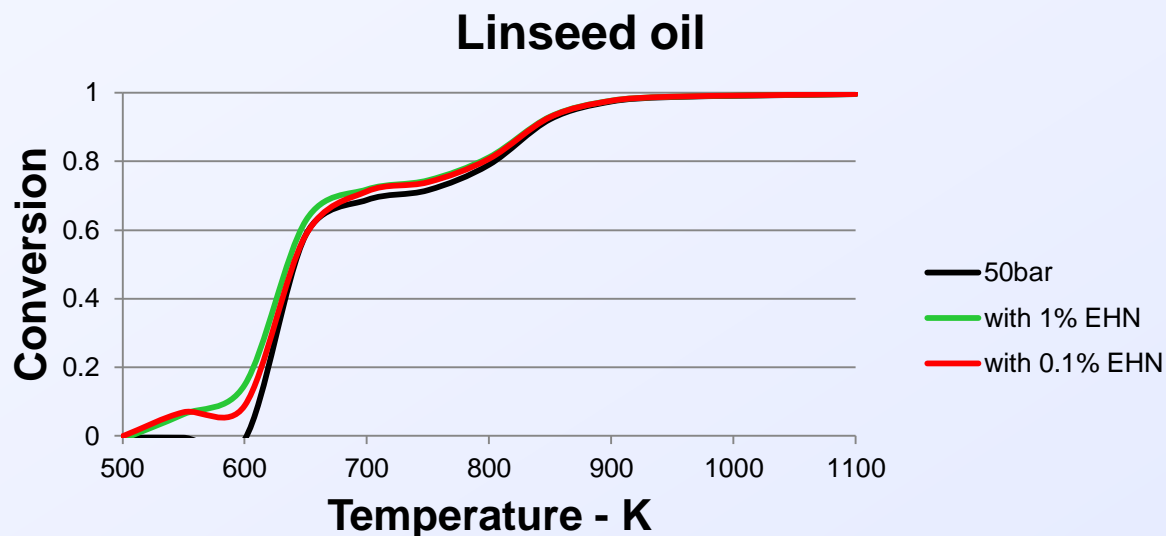


# Ethyl Hexyl Nitrate increases CN



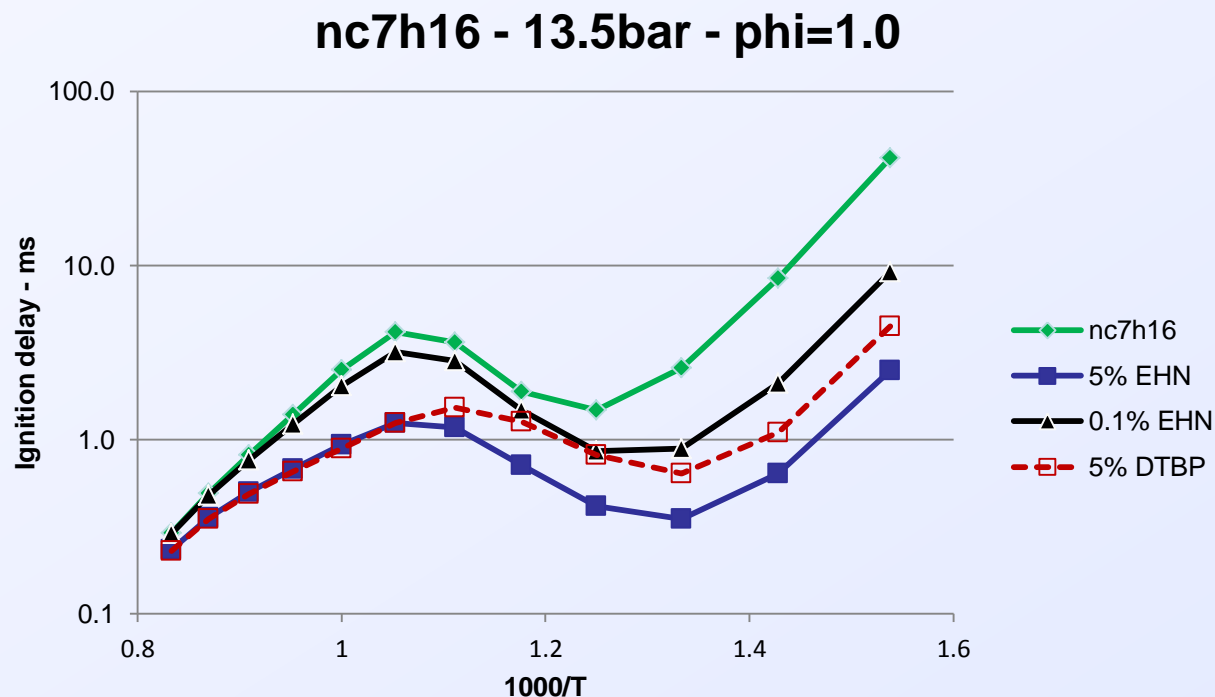
0.1% of the fuel is Ethyl Hexyl Nitrate

# More EHN has only a small incremental effect



More Ethyl Hexyl Nitrate has smaller proportional effect

# Shock tube simulations illustrate enhanced ignition from EHN and DTBP



# We can explain and model major factors that affect CN

- Most of the effects occur at low temperatures
  - $550\text{K} \leq T \leq 750\text{K}$
- Molecular structure has a big effect
  - $\text{CN}(\text{n-cetane}) = 100$
  - $\text{CN}(\text{iso-cetane}) = 15$
- Molecule chain length has a big effect
  - $\text{CN}(\text{n-heptane}) = 56$
  - $\text{CN}(\text{n-cetane}) = 100$
  - $\text{CN}(\text{methyl decanoate}) = 47$
  - $\text{CN}(\text{methyl stearate}) = 101$
- C=C double bonds have a big effect
  - Methyl stearate  $\rightarrow$  methyl linolenate    CN: 101  $\rightarrow$  23
- Effects of diesel ignition enhancers such as EHN and DTBP

# Still many reaction pathways are uncertain

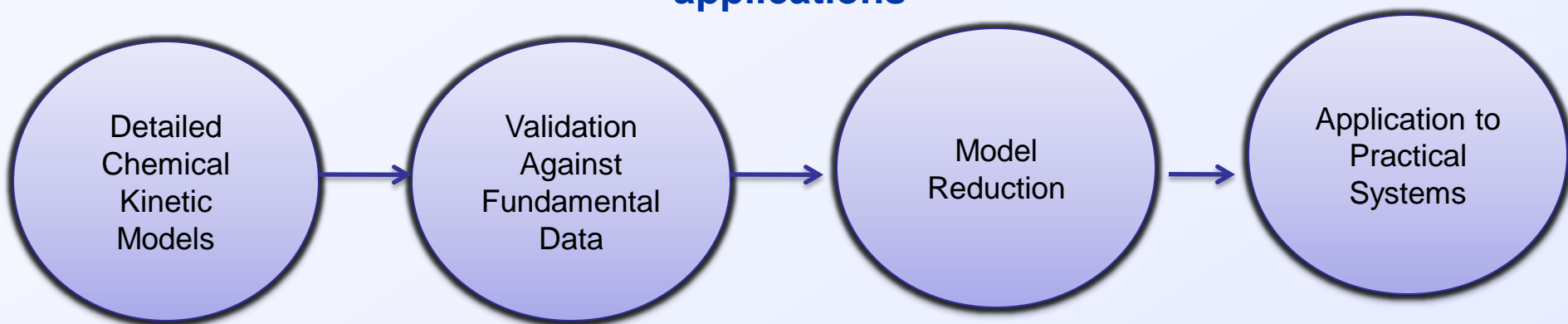
- Nobody has studied kinetics in large species with multiple C=C bonds
- Rates and products highly uncertain but important in biodiesel fuels
- Tough to do kinetics experiments (low vapor pressures)
- Many groups are doing experiments with smaller alkyl ester fuels, saturated and unsaturated.
- Little of this body of new experiments includes smaller alkyl esters with multiple C=C bonds
- Uncertainties in thermochemistry, known to have significant influences
- cis/trans issues with multiple double bonds

# Next steps

- We need to extend this analysis to aromatics, cyclo-paraffins, olefins and other fuel types
- We need mechanism validation experiments for all of these fuel types
- We need theory support for the types of reactions that we have found to be important in these systems
- In the past several years, the numbers and structures of fuels with kinetic mechanisms have grown rapidly

# Conclusions

**Validated chemistry models can eventually be used in practical applications**



**New Chemical kinetic model have been developed for:**

- Branched alkanes
- 2-methylheptane, 3-methylheptane, and 2,5-dimethylhexane
  - C8 Aromatics
  - Xylenes and Ethylbenzene
  - Gasoline Surrogates
    - Alcohols
- Butanol isomers and iso-pentanol